

CORROSION

2

Corrosion Control

third edition



edited by

L L Shreir, R A Jarman & G T Burstein



CORROSION

Volume 2

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INTRODUCTION

Corrosion Control

In Section 1.1 *corrosion* was defined simply as the reaction of a metal with its environment, and it was emphasised that this term embraces a number of concepts of which the rate of attack per unit area of the metal surface, the extent of attack in relation to the thickness of the metal and its form (uniform, localised, intergranular, cracking, etc.) are the most significant. The rate of corrosion is obviously the most important parameter, and will determine the life of a given metal structure. Whether or not a given rate of corrosion can be tolerated will, of course, depend upon a variety of factors such as the thickness of the metal, the function and anticipated life of the metal structure and the effect of the corrosion products on the environment, etc.

With metals used as construction materials *corrosion* control may be regarded as the regulation of the reaction so that the physical and mechanical properties of the metal are preserved during the anticipated life of the structure or the component. In relation to the term 'anticipated life' it should be noted that this cannot be precise, and although the designer might be told on the basis of information available at that time that the plant should last, say, 10 years, it might be scrapped much earlier or be required to give more prolonged service. It is also evident that, providing there are no restrictions on costs, it is not difficult to design a plant to last at least 10 years, but quite impossible to design one that will last exactly 10 years. Thus although under-design could be catastrophic, over-design could be unnecessarily expensive, and it is the difficult task of the corrosion engineer to avoid either of these two extremes. A further factor that has to be considered is that in the processing of foodstuffs and certain chemicals, contamination of the environment by traces of corrosion products is far more significant than the effect of corrosion on the structural properties of the metal, and under these circumstances the materials selected must be highly resistant to corrosion.

Since corrosion involves a reaction of a metal with its environment, control may be effected through either or both of the two reactants. Thus control could be based entirely on the selection of a particular metal or alloy in preference to all others or the rejection of metals in favour of a non-metallic material, e.g. by a glass-reinforced polymer (g.r.p.). At the other extreme control may be effected by using a less corrosion-resistant material and

reducing the aggressiveness of the environment by (a) changing composition, (b) removing deleterious impurities, (c) lowering temperature, (d) lowering velocity, (e) adding corrosion inhibitors, etc.

Although it has been found to be convenient to present this work in the form of two volumes entitled *Metal/Environment Reactions* and *Corrosion Control*, it is evident that this separation is largely artificial, and that a knowledge of the various types of corrosion behaviour of different metals under different environmental conditions is just as important for corrosion control as the protective treatments that have been collated in this volume.

In many structures and components the choice of a metal and alloys is based largely on their engineering properties, but it is seldom that their resistance to corrosion can be ignored completely; at the other extreme corrosion resistance may be of predominant importance, but even so the engineering properties cannot be neglected. Availability is frequently of over-riding importance, and it is quite futile to specify a particular alloy and then to find that it cannot be manufactured and delivered to the fabricators for a year or more. Fabrication technology and fabrication costs will also have to be considered, and in certain cases a more expensive alloy will be preferable to a cheaper one with adequate corrosion resistance that is more difficult to fabricate, e.g. an 18% Cr-8% Ni austenitic stainless steel is frequently selected in preference to a cheaper ferritic 17% Cr stainless steel, since the latter is more difficult to weld than the former, although its corrosion resistance may be adequate.

Costs must always be considered, but it does not follow that an inexpensive metal or alloy will prove to be the cheapest in the long term; platinum and platinum alloys are used in certain applications and apart from their high corrosion resistance have been a wise investment for the purchaser. However, mild steel, which has good mechanical properties, is readily available in a variety of forms and easily fabricated, is frequently preferred to more corrosion-resistant alloys for large structures, and its poor resistance to corrosion is counteracted by means of protective coatings, cathodic protection, conditioning the environment, etc.

Classification of Practical Methods of Corrosion Control

In 1957 the late Dr W. H. J. Vernon¹ presented an outline scheme of 'Methods of Preventing Corrosion' in which four categories were defined, i.e. (a) modification of procedure, (b) modification of environment, (c) modification of metal, and (d) protective coatings; the scheme also indicated the suitability of the method for protecting a metal in different natural environments.

Table 0.1 provides a more comprehensive scheme of methods of corrosion control, in which it has been considered appropriate to include 'Corrosion Testing and Monitoring' and 'Supervision and Inspection', since, as will be discussed subsequently, these can be of some importance in ensuring that the material, coating or procedure provides effective protection. No attempt has been made to include environments for the very good reason that a particular

method may be equally suitable for a number of environments of diverse nature, e.g. a stainless steel may be used for a high-temperature oxidising environment or for an ambient-temperature aqueous environment; cathodic protection may be used for a variety of aqueous environments ranging from fresh waters to wet-clay soils.

Table 0.1 shows the enormous scope of corrosion control, and serves to emphasise the fact that it is just as important to avoid certain features in the design of a structure as to apply a particular protective scheme, and it is also apparent from Method I that many of the factors that determine the choice of a metal or a particular protective scheme are outside the realm of metallic corrosion.

It is almost axiomatic amongst corrosion engineers that corrosion control should be given due consideration at the design stage of the structure, and much has been said and written² about stimulating *corrosion consciousness* in design engineers who normally make the decisions concerning materials selection and methods of protection. There is no doubt that the incidences of corrosion failure could be substantially reduced if due consideration were given to corrosion hazards during the design stage, a point that was emphasised strongly in the Hoar Report³. However, the design engineer is frequently too involved in the stability and proper functioning of the structure to be overconcerned about corrosion protection, particularly when hazards such as stress-corrosion cracking are unlikely to arise. It follows that all too frequently corrosion control has to be effected when the design has been finalised and at a stage when the corrosion hazards that have been inadvertently built into the structure cannot be altered, and under these circumstances considerable ingenuity has to be exercised by the corrosion engineer. Fortunately, many methods of corrosion control such as cathodic protection, conditioning the environment, protective coatings, etc. can be applied after the structure is designed and constructed, and although this is by no means an ideal situation it is one that has to be lived with.

It is evident from Table 0.1, and bearing in mind the enormous variety of materials that are now available, that the choice of a particular method for controlling the corrosion of a given system is an extremely difficult task, and it is seldom that a particular method has so many advantages that it presents the obvious and only solution to the problem when all factors are taken into consideration; frequently, the final decision is based upon a compromise between effectiveness of protection and the cost of its implementation. For heat exchangers using sea-water as a coolant a variety of alloys are available ranging from the aluminium brasses to titanium; the latter might be the obvious choice for highly polluted sea-water, but at the present the cost could be prohibitive although for certain applications (de-salination of sea-water) titanium could be a serious competitor to the cupro-nickel alloys.

The continuous development of new materials has resulted in changing attitudes towards materials selection for corrosion control, and the range of materials now available can be gauged from the Materials Selector Review⁴, which becomes considerably thicker each time it is updated. Plastics are replacing metals for a variety of applications and a recent application is the use of g.r.p. in place of metals for the construction of hulls of hovercrafts; the corrosive action of the high velocity spray of sea-water is such that very few metals are capable of withstanding it and the use of g.r.p. represents the

best combination of strength, impact resistance, rigidity, lightness and corrosion resistance.

Table 0.1 Outline of methods of corrosion control

1. Selection of materials

Select metal or alloy (or non-metallic material) for the particular environmental conditions prevailing (composition, temperature, velocity, etc.) taking into account mechanical and physical properties, availability, method of fabrication and overall cost of structure. Decide whether or not an expensive corrosion-resistant alloy is more economical than a cheaper metal that requires protection and periodic maintenance.

2. Design

If the metal has to be protected make provision in the design for applying metallic or non-metallic coatings or applying anodic or cathodic protection. Avoid geometrical configurations that facilitate corrosive conditions such as

- (a) Features that trap dust, moisture and water.
- (b) Crevices (or else fill them in) and situations where deposits can form on the metal surface.
- (c) Designs that lead to erosion-corrosion or to cavitation damage.
- (d) Designs that result in inaccessible areas that cannot be re-protected, e.g. by maintenance painting.
- (e) Designs that lead to heterogeneities in the metal (differences in thermal treatment) or in the environment (differences in temperature, velocity).

3. Contact with other materials

Avoid metal-metal or metal-non-metallic contacting materials that facilitate corrosion such as

- (a) Bimetallic couples in which a large area of a more positive metal (e.g. Cu) is in contact with a small area of a less noble metal (e.g. Fe, Zn or Al).
- (b) Metals in contact with absorbent materials that maintain constantly wet conditions or in the case of passive metals that exclude oxygen.
- (c) Contact (or enclosure in a confined space) with substances that give off corrosive vapours, e.g. certain woods and plastics.

4. Mechanical factors

Avoid stresses (magnitude and type) and environmental conditions that lead to stress-corrosion cracking, corrosion fatigue or fretting corrosion.

- (a) For stress-corrosion cracking avoid the use of alloys that are susceptible in the environment under consideration, or if this is not possible ensure that the external and internal stresses are kept to a minimum.
- (b) For a metal subjected to fatigue conditions in a corrosive environment ensure that the metal is adequately protected by a corrosion-resistant coating.
- (c) Processes that induce compressive stresses into the surface of the metal such as peening, carburising and nitriding are frequently beneficial in preventing corrosion fatigue and fretting corrosion.

5. Coatings

If the metal has a poor resistance to corrosion in the environment under consideration make provision in the design for applying an appropriate protective coating such as

- (a) Metal reaction products, e.g. anodic oxide films on Al, phosphate coatings on steel (for subsequent painting or impregnation with grease), chromate films on light metals and alloys (Zn, Al, Cd, Mg).
- (b) Metallic coatings that form protective barriers (Ni, Cr) and also protect the substrate by sacrificial action (Zn, Al or Cd on steel).
- (c) Inorganic coatings, e.g. enamels, glasses, ceramics.
- (d) Organic coatings, e.g. paints, plastics, greases.

Note. Prior to applying coatings adequate pretreatment of the substrate is essential.

Table 0.1 (continued)

6. Environment

Make environment less aggressive by removing constituents that facilitate corrosion; decrease temperature, decrease velocity*; where possible prevent access of water and moisture.

- (a) For atmospheric corrosion dehumidify the air, remove solid particles, add volatile corrosion inhibitors (for steel).
- (b) For aqueous corrosion remove dissolved O_2 , increase the pH (for steels), add inhibitors.

7. Interfacial potential

- (a) Protect metal cathodically by making the interfacial potential sufficiently negative by (i) sacrificial anodes or (ii) impressed current.
- (b) Protect metal by making the interfacial potential sufficiently positive to cause passivation (confined to metals that passivate in the environment under consideration).

8. Corrosion testing and monitoring

- (a) When there is no information on the behaviour of a metal or alloy or a fabrication under specific environmental conditions (a newly formulated alloy and/or a new environment) it is essential to carry out corrosion testing.
- (b) Monitor composition of environment, corrosion rate of metal, interfacial potential, etc. to ensure that control is effective.

9. Supervision and inspection

Ensure that the application of a protective coating (applied *in situ* or in a factory) is adequately supervised and inspected in accordance with the specification or code of practice.

*Note. For passive metals in solutions free from other oxidising species the presence of dissolved O_2 at all parts of the metal's surface is essential to maintain passivity and this can be achieved in certain systems by increasing the velocity of the solution.

There is a great deal of information available on the corrosion resistance of metals and alloys in various environments and this aspect of corrosion control has been dealt with in Volume 1. Reference should also be made to Rebal's *Corrosion Guide*⁵ which gives the corrosion resistance of metals and alloys in over 500 chemicals, to the N.A.C.E. *Corrosion Data Survey*⁶ and to *Dechema Materials Tables*⁷. However, in spite of all this information environments and/or environmental conditions will be encountered for which corrosion data is not available, and under these circumstances it will be necessary to initiate a programme of corrosion testing (Table 0.1, Method 8), which must be regarded, therefore, as an aspect of corrosion control. Corrosion testing is, of course, vitally important in ensuring that an alloy conforms to specifications, particularly when maltreatment can result in the precipitation of phases that lead to intergranular attack or to a susceptibility to stress-corrosion cracking. It is also important when conditioning the environment (control of oxygen concentration and pH, addition of inhibitors) to ensure that this is being carried out effectively by monitoring the environment and/or the corrosion rate of the metal, monitoring the potential (as in cathodic and anodic protection), etc.

Paints are one of the most important methods of corrosion control, but it is well known that many cases of failure result from inadequate surface preparation of the metal and careless application of the paint system; procedures that are often carried out under adverse or unsuitable environmental conditions by labour that is relatively unskilled. A great deal of research and

Table 0.2 More fundamental classification of corrosion control⁸

Principle of method	Part of system involved	Method of corrosion control	Examples
(a) Increase thermodynamic stability of the system	Metal	Alloy with a more thermodynamically stable metal	Additions of Au to Cu, or Cu to Ni
	Environment (aqueous)	Lower the redox potential of the solution, i.e. lower $E_{\text{eq.,c}}$ Increase the potential of the M^{z+}/M equilibrium, i.e. increase $E_{\text{eq.,a}}$	Lower a_{H^+} by raising pH, remove dissolved O_2 or other oxidising species Increase $a_{\text{M}^{z+}}$ by removing complexants (e.g. CN^- ions) from solution
	Environment (gaseous)	Remove O_2 or other oxidising gases in which the metal is unstable	Use of inert atmospheres (H_2 , N_2 , A) or of vacuo
	Metal surface	Coat with continuous film of a thermodynamically stable metal	Au coatings on Cu
(b) Metal cathodic control	Metal	Decrease kinetics of cathodic reaction	Change the nature of the cathode metal in a bimetallic couple; plate cathodic metal (Cd plating of steel in contact with Al); apply paint coatings. Reduce area of cathodic metal
		Remove cathodic impurities; ensure that anodic phases do not precipitate	Remove heavy metal impurities from Zn, Al, Mg (for use as sacrificial anodes or in the case of Zn for dry cells); ensure that CuAl_2 phase in Duralumin and carbide phase in stainless steel are maintained in solid solution
		Increase cathodic overpotential	Amalgamation of zinc; alloying commercial Mg with Mn
	Environment	Reduce kinetics of cathodic reaction	Reduce a_{H^+} , reduce O_2 concentration or concentration of oxidising species; lower temperature, velocity agitation
		Lower potential of metal	Cathodically protect by sacrificial anodes or impressed current; sacrificially protect by coatings, e.g. Zn, Al or Cd on steel
		Cathodic inhibition	Formation of calcareous scales in waters due to increase in pH; additions of poisons (As, Bi, Sb) and organic inhibitors to acids

Table 0.2 (continued)

<i>Principle of method</i>	<i>Part of system involved</i>	<i>Method of corrosion control</i>	<i>Examples</i>
(c) Increased anodic control	Metal	Alloy to increase tendency of metal to passivate	Alloying Fe with Cr and Ni
		Alloying to give more protective corrosion products	Additions of low concentrations of Cu, Cr and Ni to steel
		Introduction of electrochemically active cathodes that facilitate passivation	Additions of Pt, Pd and other noble metals to Ti, Cr and stainless steels
	Environment	Raise potential by external e.m.f	Anodic protection of steel, stainless steel and Ti
		Increase redox potential of solution	Passivation of stainless steel by additions of O ₂ , HNO ₃ or other oxidising species to a reducing acid
		Addition of anodic inhibitors	Additions of chromates, nitrates, benzoates, etc. to neutral solutions in contact with Fe; inhibitive primers for metals, e.g. red lead, zinc chromate, zinc phosphate
(d) Resistance control	Surface	Coatings of metals that passivate readily	Cr coatings on Fe
		Surface treatments to facilitate formation of passive film	Polishing stainless steel and removing Fe impurities by HNO ₃ ; chromate treatment of Al
	Surface	Coatings	Organic coatings that increase <i>IR</i> drop between anodic and cathodic areas
	Environment	Removal of water or electrolytes that increase conductivity	Design to facilitate drainage of water; drainage of soils

development followed by an extensive programme of corrosion testing is required before a paint system is incorporated in a specification or code of practice, but all this effort will be fruitless unless the work is carried out properly, and for this reason effective supervision and inspection is essential. Similar considerations apply, of course, to factory-applied coatings such as sprayed, hot-dipped and electroplated coatings.

Finally, it is necessary to point out that although a particular method of corrosion control may be quite effective for the structure under consideration it can introduce unforeseen corrosion hazards elsewhere. Perhaps the best example is provided by cathodic protection in which stray currents (interaction) result in the corrosion of an adjacent unprotected structure or of steel-reinforcement bars embedded in concrete; a further hazard is when the cathodically protected steel is fastened with high-strength steel bolts, since cathodic protection of the latter could result in hydrogen absorption and hydrogen cracking.

More Fundamental Classification

Any fundamental classification of corrosion control must be based on the electrochemical mechanism of corrosion, and Evans diagrams may be constructed (Fig. 1.27, Section 1.4) illustrating

- (a) Decreasing the thermodynamics of the corrosion reaction.
- (b) Increasing the polarisation of the cathodic reaction (cathodic control).
- (c) Increasing the polarisation of the anodic reaction (anodic control).
- (d) Increasing the resistance between the cathodic and anodic sites (resistance control).

Tomashov⁸ has produced a detailed scheme of control based on the electrochemical mechanism of corrosion, which has been set out in an abridged and modified form in Table 0.2. However, although more fundamental than Table 0.1, it has several limitations, since it is not always possible to define the precise controlling factor, and frequently more than one will be involved. Thus removal of dissolved oxygen (partial or complete) from an aqueous solution reduces the thermodynamics of the reaction and also increases the polarisation of the cathodic reaction, and both contribute to the decrease in the corrosion rate although the latter is usually the more significant.

The primary function of a coating is to act as a barrier which isolates the underlying metal from the environment, and in certain circumstances such as an impervious continuous vitreous enamel on steel, this could be regarded as thermodynamic control. However, whereas a thick bituminous coating will act in the same way as a vitreous enamel, paint coatings are normally permeable to oxygen and water and in the case of an inhibitive primer (red lead, zinc chromate) anodic control will be significant, whilst the converse applies to a zinc-rich primer that will provide cathodic control to the substrate.

Tomashov considers that greater effectiveness of control may be achieved by using more than one method of protection, providing that they all affect the same controlling factor. Thus chromium is alloyed with iron to produce an alloy that relies on passivity for its protection, and passivation can be

enhanced by raising the redox potential of the solution, by alloying it with platinum or palladium, or by raising the potential by an external source of e.m.f. However, there is no reason why stainless steel should not be cathodically protected, and although this appears to be a contradiction it is sometimes necessary, particularly when the stainless steel is in contact with a mild steel.

Conclusions

1. The selection of a particular method of corrosion control is by no means simple and a variety of factors will have to be considered before a final decision is taken, particularly when there is no previous experience of the corrosiveness of the environment or the alloy under consideration.

2. It is just as important to avoid design features in the structure that facilitate corrosion as to apply positive protective schemes, an aspect of corrosion control that is frequently neglected.

3. Corrosion testing and monitoring, and supervision and inspection are essential aspects of corrosion control.

L. L. SHREIR

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9 DESIGN AND ECONOMIC ASPECTS OF CORROSION

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9.1 Economic Aspects of Corrosion

The Cost of Corrosion*

Deterioration as a result of corrosion is often accepted as an unavoidable fact of life, and this has led to a widespread lack of awareness of the importance of economic aspects of corrosion. Thus a detailed survey of corrosion and protection in the UK revealed that only a limited number of firms were sufficiently corrosion conscious to be able to estimate the costs of corrosion to their own activities¹. Many were unable to supply any information, the cost of corrosion being hidden as, for example, general maintenance. For this, and other reasons, calculation of the economic significance of corrosion on a national scale is very difficult, and any figures for the annual cost to a country cannot be precise. Estimates indicating the order of magnitude of expenditure in relation to Gross National Product (GNP) are, however, of interest in showing the economic significance of corrosion, and as a basis for assessing possible savings that could be made.

Estimates were made by Uhlig² in the USA. Worner³ in Australia, and Vernon⁴ in the UK, in which the cost of protection and prevention were added to the cost of deterioration due to corrosion. These early estimates were made by individual scientists from cost information from new major industries scaled up to a national level, and were of the order of 1–1.5% of GNP. More detailed estimates were subsequently made by the Committee on Corrosion and Protection (the Hoar Committee)¹ in the UK, and Payer *et al.*⁵ for the National Bureau of Standards in the USA. The later estimates were around 3.5–4% of GNP, the higher figure reflected factors not covered in the earlier surveys, which were, moreover, based on organisations which had probably already taken action to minimise their corrosion costs. Estimates have since been made for other European countries which tend to confirm the higher figure.

The detailed surveys^{1,5} made 15 to 20 years ago led to greater awareness of the significance of corrosion which undoubtedly led to improvements, particularly in some fields where the situation was poor. Thus, improved protective systems and increased use of plastics in consumer items and

*Most costs quoted in this chapter are historical costs taken from the source indicated and therefore relate to different times over a period of about 40 years. No attempt has been made to correct for inflation, which could be misleading, as is discussed in the later part of the chapter.

automobiles (together with more resistant materials for exhausts in the latter) have lead to significant savings. Similarly, wider appreciation of the benefits of shop priming, of galvanising and similar treatments, and the value of high-build paints, have lead to major improvements in practices for structural steelwork.

On the other hand, the Hoar Committee's estimate for the UK did not include some significant factors, and some costs that were considered have increased in real terms since the estimates were made. Larger plants and structures are more common, and even when there is no increase in size more intensive use of equipment is demanded. As a result, the real cost of downtime or unavailability, and of dislocation to users of, for example, motorway viaducts while repairs are made, have increased appreciably. Moreover, maintenance and rectification are labour intensive activities, and hence particularly susceptible to the effects of inflation. The increases probably outweigh the savings mentioned, and the current cost of corrosion in the UK is probably around 4% of GNP. As future savings depend on the improvement being maintained despite pressures to reduce first costs, a sound economic approach to corrosion is no less important than it was in 1970.

The figure of 4% of GNP is probably reasonable for other developed countries, although differences may exist because the mix of industries is not the same—see the data in Table 9.1. Differences in climate, and the level of industrial pollution etc. can be very significant. The cost of corrosion in terms of GNP may well be higher in some less developed countries, although it is probably less in the least developed countries.

The expenditure, and potential savings estimated by the UK Committee on Corrosion¹ for a variety of industries are shown in Table 9.1. The savings shown are those which could be made by better use of available knowledge, and do not include the potential benefit of future research and development. The costs referred to are mainly those arising in the industries concerned, or, in certain cases, sustained by users of the products because of the need for protection, maintenance and replacement of the materials of construction. In the oil and chemical industries the costs of using corrosion resistant

Table 9.1 Expenditure and estimated potential savings in various industries in 1971¹

<i>Industry or agency</i>	<i>Estimated cost (£M)</i>	<i>Estimated potential saving</i>	
		<i>(£M)</i>	<i>Expressed as % of estimated cost</i>
Building and construction	250	50	20
Food	40	4	10
General engineering	110	35	32
Government depts. and agencies	55	20	36
Marine	280	55	20
Metal refining and semi-fabrication	15	2	13
Oil and chemical	180	15	8
Power	60	25	42
Transport	350	100	29
Water supply	25	4	16
<i>Total</i>	1365	310	23

materials, where the conditions of service make this essential, were included. Indirect consequential losses, such as loss of goodwill, which in some industries can be very high, were not included.

At first sight these costs appear to be far too high to be attributable to corrosion and it is worthwhile considering the indirect expenses which add so considerably to the total.

Loss of Production

The repair or replacement of a corroded piece of equipment may cost relatively little, but while the repair is being carried out a whole plant may shut down for a day or more. In a small plant it may sometimes be more profitable to use a cheap material and replace it regularly than to use a more expensive material with a longer life. In a large integrated factory, however, maintenance work on one plant may cause loss of production from several others. It then becomes essential to reduce periods when the plant has to be shut down to a minimum. Thus the choice of materials may be dictated by requirements beyond the individual units, and the higher cost of corrosion resistant alloys justified in return for longer maintenance-free periods. The replacement of a corroded boiler or condenser tube in a modern power station capable of producing 500 MW could result in losses in excess of £20 000/h. Similar examples could be quoted for oil, chemical and other industries.

Reduction of Efficiency

The accumulation of corrosion products can reduce the efficiency of operating plant. It has been estimated that the extra pumping costs due to clogging of the interior of water pipes amounted to £17 000 000/year in the United States⁶. Pipelines for conveying North Sea Gas are painted on the interior to reduce the costs of pumping. Other examples of loss of efficiency are the reduction of heat transfer through accumulated corrosion products and the loss of critical dimensions within internal combustion engines. The corrosion within internal combustion engines is caused by both the combustion gases and their products and has been claimed to be more detrimental than wear².

Product Contamination

Some industries, notably the fine chemicals and parts of the food processing industry, cannot tolerate the pick-up of even small quantities of metal ions in their products. To avoid corrosion, plants often have to incorporate lined pipework and reaction vessels, while in a slightly less demanding situation whole plants are made of an appropriate grade of stainless steel. The capital investment in these industries is thus considerably increased due to the necessity to avoid corrosion.

Corrosion that would otherwise be trivial can result in staining or discoloration of product and cause serious losses; it may be some time before the cause is finally identified.

Maintenance of Standby Plant and Equipment

Regular shutdowns cannot be tolerated in large integrated factories and replacement sections of plant have to be maintained in readiness to operate when corrosion failure occurs. This method of dealing with corrosion can lead to a considerable increase in capital investment.

General Losses

The indirect consequential losses resulting from corrosion are less amenable to calculation but may well outweigh the direct costs. The unpredictable failure of critical parts of industrial equipment, aircraft or other means of transport can cause accidents costing both lives and money. The cost in human life and suffering cannot be assessed but the material damage alone probably amounts to many millions of pounds annually. The degree of corrosion involved may be very slight, such as pitting penetration of a washer or a tube, but the ramifications are large. Surface oxidation of an electrical contact has caused the failure of expensive and sophisticated equipment¹. Thus the cost of corrosion can be, and often is, many orders of magnitude higher than the value of the material reacted.

Costs Associated with Design

Corrosion decisions are only one part of the engineering design process, and it is important that these and related decisions do not cause undue delay⁷. Delay can seriously damage the profitability of the project by increasing interest charges before any income from production; it may also mean that a market opportunity is lost. These effects are on the whole project: a delay associated with a corrosion decision can lead to costs much greater than those directly associated with corrosion.

The overall design process depends on the use of codes of practice and specifications, and to an increasing extent on computer-based techniques. The potential cost of delay is therefore a strong incentive to the use of 'standard' solutions, compatible with the codes of practice⁷, and to develop ways of using the computer to provide corrosion information and knowledge⁸, or to improve prediction of corrosion behaviour⁹. Note that both points relate to the use of existing knowledge, in the sense of an important conclusion of the Hoar Report¹.

The difficulty of predicting corrosion behaviour in a complex situation, and of determining what changes in conditions are likely during the required life of an item, makes deliberate overdesign a common approach. An alloy or protective system more resistant than is actually required may be used, or thicker sections than needed for mechanical reasons adopted, giving a

'corrosion allowance'. A corrosion allowance can be cheaper than a more resistant alternative, and other forms of overdesign may be justifiable in comparison with the cost of proving a cheaper solution. Overdesign is not, therefore, necessarily unsound in economic terms, but its cost may be hidden, and can be much greater than is realised. If a new plant is basically similar to a previous one, in which a given alloy has given no problems, the same alloy is often chosen almost without thought. However, the original selection might have been overconservative, deliberately or otherwise, or the conditions may actually be less severe than were assumed in the first plant. The costs of such hidden overdesign can be large; an unnecessarily expensive alloy could increase first cost by almost an order of magnitude.

Costs Associated with Novel Solutions

Accepted solutions are usually covered by specifications and codes of practice. These documents are important for three reasons: they form part of the contract; they define methods of design and fabrication proven by experience; and they act as a means of communication between the parties involved in design, fabrication, construction and inspection. There is a strong incentive to use 'standard' solutions as unexpected problems or misunderstandings are less likely to occur than if a novel solution is attempted; such problems lead to the cost of rectification, but the delay that they cause is usually more important¹². Consequently project managers are often reluctant to be the first to use a novel solution.

This does not, of course, mean that improvements should not be attempted. It is important, however, that corrosion scientists and technologists appreciate that significant 'hidden' costs may arise when a novel solution is considered. A considerable effort is needed to ensure that the information needed by the design engineer is available when it is needed, and that all the parties concerned understand what is required. The documentation needed can be large, and requires an input from a number of disciplines; even when it has been produced, much more effort from experienced staff is likely to be needed than if a 'standard' solution were used.

Savings

The national costs associated with corrosion have been described in terms of the industries concerned, and the ways in which this expenditure can arise. A major interest is in the extent to which this substantial cost can be reduced, and how this can be attempted.

Table 9.1 includes estimates of potential savings published in 1971. The variations in the ratio of savings to costs are in part due to differences in the extent to which severely corrosive environments are characteristic of the industry concerned. However, the differences also reflect the uneven level of corrosion awareness when the estimates were made¹, and as significant improvements in practices have occurred, the detailed figures do not entirely represent the current situation. For example, corrosion of cars is now a much smaller problem than it was in 1970. The automobile industry is also an

example where the main savings have been made by customers rather than within the industry. The improvement is largely due to widespread recognition that corrosion is avoidable, resulting in pressure from outside the industry; customers recognise that it is sensible to accept higher first cost for a product with lower maintenance cost and higher resale value. Corrosion protection has become a feature of manufacturers' competition.

The improvements made have been real but, as has been pointed out, some costs not directly associated with deterioration of metal have increased. The potential savings are substantial, and are not confined to industries where corrosion is an obvious problem. In the larger chemical and oil companies corrosion and protection are the responsibility of 'materials engineering' sections, which include specialists in other materials problems as well as in corrosion. These sections are part of the overall engineering organisation, which makes possible the multidisciplinary approach needed to ensure that corrosion advice takes account of other materials aspects, the design methods used in the company, and economic factors. In businesses where general materials problems do not justify a specialist section, corrosion problems are necessarily dealt with on a part time basis by staff of other engineering or scientific backgrounds. External corrosion consultants or advisory services can be a valuable additional resource.

In general, decisions about corrosion and protection are part of wider engineering decisions, and the overall responsibility lies with management, e.g. with a project or maintenance manager, who has at best limited knowledge of corrosion. It is vital, therefore, that corrosion specialists understand how to provide advice in such a way that the manager can understand the significance and be able to act on it¹⁰. While any engineering decision depends on technical factors, choices between alternatives, and the decision whether a project will proceed, are made on economic grounds. However sound technically, advice from a corrosion specialist is only likely to be accepted willingly by the manager if it includes economic factors. It is also essential that corrosion advice takes account of the design procedures being used, aspects such as fabrication or availability, and that it does not cause unacceptable delay.

Assessment of Economic Factors

While almost any corrosion problem can be solved or avoided, it is vitally important from a commercial point of view that the economics of corrosion prevention are taken into account. This necessitates evaluation of initial protection costs together with maintenance charges throughout service life. This is very important when alternative protection schemes are available and will often reveal that an initial 'cheap' scheme can in reality prove to be very expensive.

The cost of protection of steelwork in a mild industrial atmosphere has been compared for a number of protection schemes¹¹ and the relevant data are shown in Table 9.2. The difference in aggregate costs illustrates the importance of considering protection on a whole life rather than on an initial cost basis; particularly when maintenance involves a labour intensive operation such as painting.

Table 9.2 Comparative schemes for protecting steelwork (27.4 m²/t)

<i>Protective scheme</i>	<i>Initial cost (£/t)</i>	<i>Maintenance scheme</i>	<i>Cost of each maintenance (£/t)</i>	<i>Aggregate cost over 24 years (£/t)</i>
1. Auto grit blast, hot galvanise (0.20 mm)	29.5	None	—	29.5
2. Pickle, galvanise (0.10 mm), 2 coats of paint (one on site)	35.0	Brushdown, spot prime, 1 top coat—after 12 years	13.7	48.7
3. Pickle, galvanise (0.10 mm)	22.0	Brushdown, prime, 1 top coat—after 12 years	17.1	39.1
4. Wire-brush, 3 coats of paint (two on site)	23.9	Brushdown, spot prime, 2 top coats—4 year intervals	20.2	124.9
5. Auto grit blast, 4 coats of paint (two on site)	35.2	Brushdown, spot prime, 1 top coat—8 year intervals	12.4	60.0

Expenditure on corrosion prevention is an investment and appropriate accountancy techniques should be used to assess the true cost of any scheme. The main methods used to appraise investment projects are payback, annual rate of return and discounted cash flow (DCF). The last mentioned is the most appropriate technique since it is based on the principle that money has a time value. This means that a given sum of money available now is worth more than an equivalent sum at some future date, the difference in value depending on the rate of interest earned (discount rate) and the time interval. A full description of DCF^{12,13} is beyond the scope of this section, but this method of accounting can make a periodic maintenance scheme more attractive than if the time value of money were not considered. The concept is illustrated in general terms by considering a sum of money P invested at an interest rate of $r\%$ per annum that will have the value $P \left(1 + \frac{r}{100}\right)^n$ after n years. Therefore the net present value (NPV) of a sum of money to be spent in the future is reduced by the interest the money can earn until the expenditure is required, hence

$$\text{NPV} = \frac{P}{\left(1 + \frac{r}{100}\right)^n}$$

A consideration of the costs of the protective Schemes 1 and 3 given in Table 9.2 indicates that the latter is significantly more expensive than the former, and it is of interest, therefore, to apply the concept of the time value of money to these two schemes for 1 t of steel processed.

1. In Scheme 1 the company will spend £29.50 immediately, but will incur no further expense.

2. In Scheme 3 it will spend £22.00 immediately, and can invest the money saved—£29.50—£22.00 = £7.50 at, say, 8% for 12 years, which will yield approximately £18.90. It will then have to spend £17.10 on painting, but

even so there will be a bonus at the end of 12 years of $\pounds 18.90 - \pounds 17.10 = \pounds 1.80$ as compared to Scheme 1.

3. Alternatively, for Scheme 3, in order to have $\pounds 17.10$ in 12 years time the company need invest only $\pounds 6.79$ immediately so that the total outlay will be $\pounds 22 + \pounds 6.79 = \pounds 28.79$, which again is a lower outlay than that for Scheme 1.

Thus it can be seen that although the aggregate cost indicates Scheme 1 to be the cheaper, it is the more expensive when account is taken of the time value of money.

Inflation

Inflation increases costs arising in the future; this can make an alternative which is more expensive initially, but has lower maintenance costs, more attractive. In effect, it reduces the effective interest rate in a DCF calculation. This can be taken into account by using a variation of the above equation. If the annual inflation rate is $i\%$, then

$$NPV = P \frac{(1 + i/100)^n}{(1 + r/100)^n}$$

This equation should be used with care. Inflation rates can change substantially, and are difficult to predict over a long period; when assumptions can cause serious errors. Moreover, the effect of inflation on different items may not be the same; for example, labour intensive activities generally have a higher inflation rate than the cost of materials. It may, therefore, be misleading to use a single inflation rate for all the costs in a calculation, whereas a single interest rate is usually valid.

Technological changes or changes in production volume reflecting the popularity of an alloy or protective treatment as confidence is gained in its use may reduce, or even reverse, the effect of inflation on some costs. In combination with inflation, these factors can greatly alter the economic order of merit of possible solutions over even a short period. Consequently, decisions should always be based on up-to-date information, and past comparisons of alternatives regarded with some suspicion.

Types of Assessment

Most examples of economic assessments in the corrosion literature are comparisons of similar artefacts in different materials, or of different protective schemes on the same artefact. The assessments in which a corrosion specialist is directly involved are usually of this type. The items concerned are well defined so that reliable costs can be sought, e.g. by quotations.

A recent NACE publication devoted entirely to the economic aspects of corrosion control contains several worked examples applicable to a number of industries¹⁴. These examples serve to illustrate that anti-corrosion procedure and materials should be selected on economic grounds, and not solely on performance grounds. In presenting a proposal to management,

the corrosion technologist should show that a thorough investigation of possible solutions has been made in terms of both equipment and expense, and highlight the solution offering the greatest economic advantage to the company¹⁵.

Corrosion can, however, be a factor in another type of assessment, which is arguably more important. It could influence important decisions about the whole project, taken at an early stage in the overall design process, which are concerned with the fundamental basis of the project rather than with corrosion aspects directly. In a major project, feasibility assessments in the initial stages are used to decide between possible alternatives, later effort being concentrated on one or two preferred options. If corrosion considerations are relevant they can influence the economics of the project as a whole, and have a much larger effect than in the first type of assessment.

For example, in the oil and chemical industries, the choice between possible processes may depend, in part, on the range of conditions which possible alloys can withstand. A more resistant alloy could allow conditions which are more severe but which permit greater efficiency in the chemical process, allowing the size of the equipment to be reduced. The cost of the plant could thus be reduced by using an alloy which is much more expensive on a weight-for-weight basis. Alternatively a more resistant alloy might permit greater operating flexibility, or eliminate the need for control systems to ensure that operating conditions remain within the limits a cheaper alloy can withstand. Analogous situations can arise in other fields. The choice of materials, or protective systems, is a factor in the decision whether a bridge should be in steel or concrete, and between basic types of steel bridges.

Assessments of this type often involve comparison of artefacts which are substantially different, but which will serve the same purpose. The items concerned are not well defined, and the costs will not be incurred for some time; accurate costing is difficult. A multidisciplinary approach is necessary, and a large design organisation will normally have specialist estimating sections possessing data based on recent purchases. Feasibility estimates cause more problems in smaller organisations, and quotations may have to be sought from potential suppliers.

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9.2 Corrosion Control in Chemical and Petrochemical Plant

Corrosion control in chemical and petrochemical plant is exercised in five distinct phases (Fig. 9.1) through the life of the plant, as follows:

1. Plant and process design, where the materials of construction, equipment design, process conditions and recommended operating practice can all be influenced to minimise the risk of corrosion. This is the most important phase.

In large companies an internal project team may design the plant, otherwise contractors provide the design. In either case, the corrosion engineer must be involved from the inception of the project. Otherwise, the materials of construction will have to be chosen to satisfy process

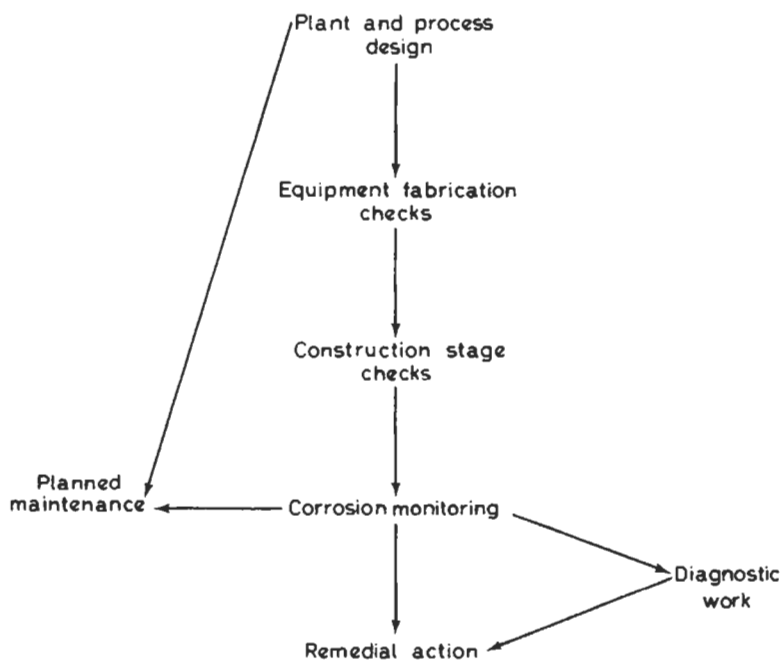


Fig. 9.1 Phases of corrosion control in chemical plant

conditions which may have been decided upon without consideration of the economic balance between process efficiency and capital cost of the plant. The importance of a continuing dialogue between the corrosion engineer and the other disciplines in the project team cannot be emphasised too strongly.

Contractor designs will be in the context of a competitive bidding situation and in-company checks of the design should cover not only design errors but also cases where calculated risks have been taken, which may not, however, be acceptable to the operating company.

The effort required to specify the materials schedule for a new plant or to check a design very much depends on how much experience there is of similar or identical units in operation. Factors such as process conditions and raw material sources are taken into consideration before extrapolating the experience of another unit.

2. Fabrication of the equipment for the plant and plant construction. An inspection system to ensure that fabricators are working to design codes and that their quality-control systems are operating effectively, is of considerable value. At the construction stage, checks are made for materials correctly specified but wrongly supplied, on-site welding quality, heat treatments carried out as specified and for damage to equipment especially where vessels have been lined.

When specifying equipment to fabricators, it should be remembered that equipment may well lie exposed on-site before erection and temporary corrosion protective measures should be considered. Any equipment precommissioning treatments specified by the design, e.g. descaling, must be carried out.

Such points of detail can make for a smooth start-up and minimum trouble during the early operational period of a new plant.

3. Planned maintenance or regular replacement of plant equipment to avoid failure by corrosion, etc. is an essential adjunct to design, and constitutes the third phase of control. The design philosophy determines the emphasis placed on controlling corrosion by this means, as opposed to spending additional capital at the construction stage to prevent corrosion taking place at all. Where maintenance labour costs are high or spares may be difficult to procure, a policy of relying heavily on planned maintenance should be avoided.
4. Even with all these checks on design, fabrication and construction, errors are made which, with maloperation and changes in process conditions during the lifetime of the plant, can all lead to corrosion. The fourth phase of control therefore lies in monitoring the plant for corrosion in critical areas. Corrosion monitors should be regarded as part of plant instrumentation and located in areas of high corrosion risk or where corrosion damage could be particularly hazardous or costly. Monitoring should include a schedule of inspections once the plant is commissioned.
5. Corrosion monitors by themselves only warn of corrosion and must be coupled with the fifth phase of control, viz. remedial action, to be effective. In some cases of corrosion the remedial measure is known or easily deduced, but in others diagnostic work has to precede a decision on remedial action.

Phase One — Plant and Process Design

The factors influencing the final choice of design are summarised in Fig. 9.2.

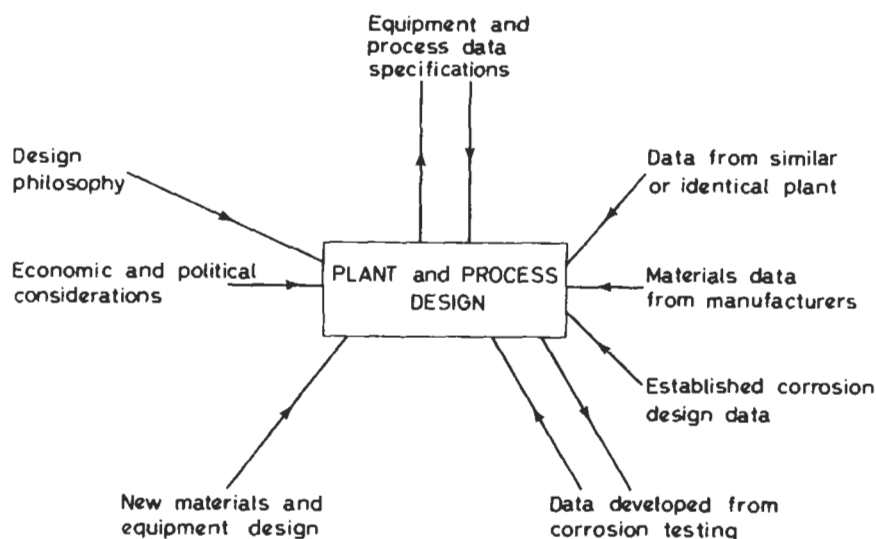


Fig. 9.2 Factors influencing plant and process design

Design Philosophy

The chemical and petrochemical industries are highly capital intensive and this has two important implications for the plant designer. Before the expenditure for any plant is approved, a discounted cash flow (DCF) return on capital invested is projected (Section 9.1). The capital cost of the plant is a key factor in deciding whether the DCF return is above or below the cut-off value used by a company to judge the viability of projects. Thus, there is always strong pressure on the materials engineer not to 'overspecify' the materials of construction.

Conversely, however, the cost of downtime can be very high and this creates a 'minimum risk' philosophy which runs contrary to the capital cost factor. The balance between these two forces has to be clearly stated to allow the materials engineer to operate effectively.

The choice of material from the viewpoint of mechanical properties must be based on design conditions. However, from a corrosion standpoint it must be realised that the design conditions are limiting values and that for most of its life the equipment will operate under 'process conditions'. For the decision on the requisite corrosion-resistance properties it is necessary to examine, by means of an operability study, how far process conditions may deviate from the normal and how often and for how long. The operability study is carried out using a line diagram for the projected plant.

The design life of the plant has to be stated so that corrosion allowances may be calculated:

$$\text{Corrosion allowance} = \text{Design life} \times \text{Expected annual corrosion rate}$$

This calculation assumes, of course, that corrosion is uniform. Finally, implicit in the design will be boundary conditions on the way the plant can be run, outside of which the risk of corrosion is high. These should be clearly set out in the operating manual for the plant.

Influence of Process Variables

The rate of a chemical reaction is influenced by pressure, temperature, concentration of reactants, kinetic factors such as agitation, and the presence of a catalyst. Since the viability of a plant depends not only on reaction efficiencies but also on the capital cost factor and the cost of maintenance, it may be more economic to alter a process variable in order that a less expensive material of construction can be used. The flexibility which the process designer has in this respect depends on how sensitive the reaction efficiency is to a change in the variable of concern to the materials engineer.

Where, for example, chloride stress-corrosion cracking is a risk the process temperature becomes a critical variable. Thus it may be more economic to lower the process temperature to below 70°C, a practical threshold for chloride stress-corrosion cracking, than to incur the extra expense of using stress-corrosion cracking-resistant materials of construction.

Pressure has less influence on corrosion rates than temperature in most cases of aqueous corrosion, although it has a large effect on some forms of gaseous corrosion at high temperatures, e.g. hydrogen attack¹. However, impingement attack is influenced by pressure in specific instances. Thus, when a gas is dissolved under pressure, and the pressure is reduced (let-down) gas bubbles are released which can contribute significantly to impingement attack if released into a high velocity stream. Pressure let-down in such cases should take place where the velocity of the liquid stream is low.

An example where reactant concentration is solely governed by corrosion considerations is in the production of concentrated nitric acid by dehydration of weak nitric acid with concentrated sulphuric acid. The ratio of HNO₃:H₂SO₄ acid feeds is determined by the need to keep the waste sulphuric acid at >70% w/w at which concentrations it can be transported in cast-iron pipes and stored after cooling in carbon-steel tanks.

Equipment Design

A recent survey by du Pont on all failures in their metallic piping and equipment taking place during a 4-year period showed corrosion accounting for 55% of total failures. Table 9.3 lists the major causes of corrosion failure in this wide ranging survey.

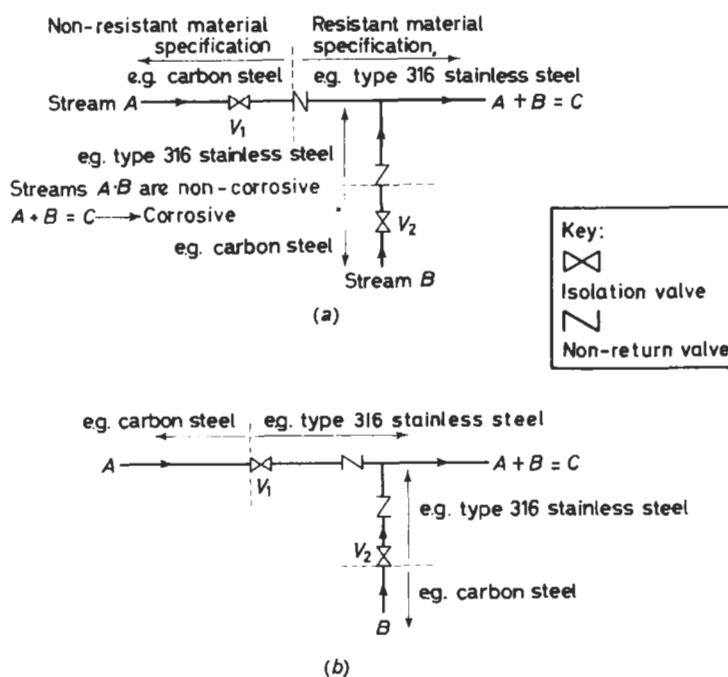
For this one company stress-corrosion cracking alone cost £2M annually and the corresponding figure for the US chemical industry was £13M³.

Some general points can be made about equipment design in connection with the more important types of corrosion.

Table 9.3 Corrosion failures analysed by type (after du Pont (1968 to 1971))

Type of corrosion	Failure rate (average %)	
General	15.2	
Stress-corrosion cracking	13.1	
Pitting	7.9	All other types < 1%
Intergranular	5.9	
Erosion/corrosion	3.8	
Weld corrosion	2.5	

General corrosion If the rate of general corrosion of a particular material in a duty is well enough characterised at the design stage, then the designer can, in some instances, use a corrodible material of construction with a suitable corrosion allowance. There are limitations to this approach. Thus, while a corrosion allowance of 6 mm on the shell of an exchanger is common practice, to make this allowance on the tube wall thickness is not practical and either a more resistant tubing material is used, or planned retubing of the unit is accepted as part of the design. This may mean carrying a spare installed exchanger or a spare tube bundle. Overall economics dictate the course to be taken.

**Fig. 9.3** Incorrect (a) and correct (b) designs where there is a sharp change in corrosivity

Corrosion with the formation of insoluble corrosion products may be unacceptable where heat-transfer equipment is concerned. Fouling by corrosion products has to be allowed for when sizing the equipment and the extra cost of using resistant material may not be as great as the increased cost of a larger exchanger in the less resistant material plus the cost of downtime to clean fouled surfaces.

Product purity specifications determine how much soluble corrosion product can be tolerated.

In many plants, one section of a process will be relatively non-corrosive, allowing cheap materials of construction to be used, while the following section will be very corrosive, necessitating more corrosion-resistant materials. The interface between the two sections has to be carefully designed to avoid corrosion in the first section at a shutdown when there may be some backflow from the corrosive section. Figures 9.3*a* and 9.3*b* show an incorrect and a correct design, respectively. The basic principle here is that a non-return valve should not be used as a means of isolating a section of the plant. Obviously, in this case, the operating manual should include instructions to close the valves V_1 and V_2 if the flow is stopped for any length of time.

A common case where intense general corrosion is experienced in a very restricted section of plant is where an acidic vapour is condensing. As a vapour the acid is usually non-corrosive, but when condensed it can only be handled in expensive materials. Another variation on this theme is that only at the region of initial condensation is there a corrosion problem, either the condense/reboil condition being particularly corrosive or else corrosion only takes place at or near the boiling point. Several variations in design are possible to cope with these situations:

1. Where the acid condensate is corrosive, neutralisers, e.g. ammonia or neutralising amines, can be injected into the vapour stream to co-condense with the acid vapour. This is the practice with the overheads of a crude oil pipestill (Fig. 9.4).
2. Where the corrosion problem is limited to the condense/reboil situation, i.e. where, due to variations in vapour temperature (or temperatures of the surfaces with which the condensate can come into contact), the condensate reboils, the answer may be to use resistant material at

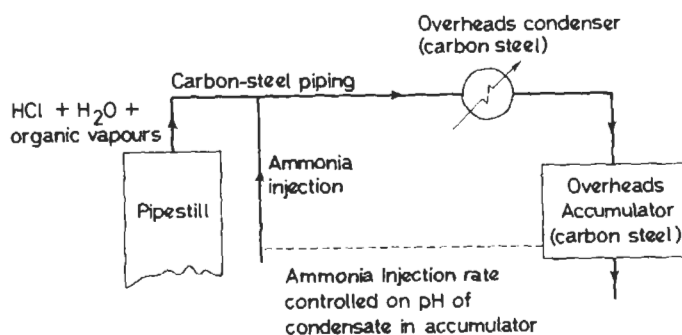


Fig. 9.4 Corrosion control in the overheads system of a crude distillation unit

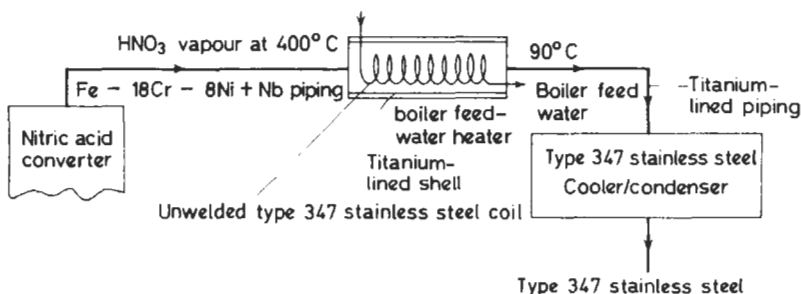


Fig. 9.5 Materials design to control corrosion in a nitric acid plant

the critical region. This expedient is adopted in condensing nitric acid vapour (Fig. 9.5). Condensation first occurs in the boiler feed-water heater. The coil-carrying boiler feed water is weldless Fe-18Cr-8Ni + Nb (type 347) to avoid attack on welds. Condensed acids drip off the coils onto the shell where they can reboil – a severe corrosion condition – the shell is therefore titanium lined.

- Where the acid condensate is corrosive and neutralisers cannot be used, then a condenser of resistant materials has to be employed. However, by steam tracing the lines leading the vapour to the condenser, premature condensation can be avoided (Fig. 9.6) and in consequence a cheaper material may be used.

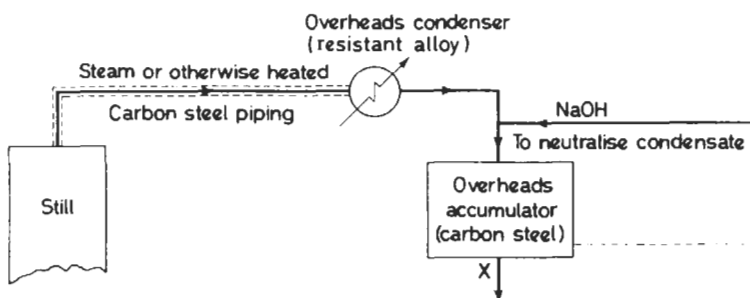


Fig. 9.6 Method of preventing corrosion by premature condensation of acidic vapours. pH measured continuously at point X automatically controls flow of sodium hydroxide

Localised corrosion The various forms of localised corrosion are a greater source of concern to the plant designer (and operator) since it is usually difficult to predict an accurate rate of penetration, difficult to monitor, and consequently can be (especially in the case of stress-corrosion cracking) catastrophically rapid and dangerous.

Stress-corrosion cracking (Section 8.10) New metal/environment combinations which produce stress-corrosion cracking are continually being found. Combinations discovered in service in recent years include titanium in red fuming nitric acid; carbon steel in liquid anhydrous ammonia⁴ and in

carbonate solutions containing arsenite as a general corrosion inhibitor⁵; and CO-CO₂-H₂O systems. Also, polythionic acid has been identified as the specific environment in several cases of the stress-corrosion cracking of stainless steel in service. Chloride stress-corrosion cracking of stainless steels is a continuous source of trouble. Almost invariably it is caused by the concentration of chlorides from a bulk electrolyte which by itself would not cause cracking. The designer has, in theory, four degrees of freedom to avoid the problem:

1. Stress relief—although success is claimed for stress relief at 900°C in alleviating the problem of chloride-induced stress-corrosion cracking, there is considerable doubt that, except in cases of marginal risk, it is a reliable method of preventing stress-corrosion cracking of austenitic stainless steels. Working stresses would appear to be sufficient to cause cracking.
2. Avoiding situations that increase the chloride concentration—some circumstances in which this can occur in practice are listed below, and it can be seen that control is difficult to ensure.
 - (a) Under deposits on heat-transfer surfaces.
 - (b) At a vapour/liquid interface in contact with a heat-transfer surface.
 - (c) At a leakage point where evaporation of leaking liquid takes place, e.g. at a leaking joint.
 - (d) Where liquid boils in a restricted space (e.g. a tube/tubeplate crevice), a thermowell, level control instruments, or in a condense/reboil situation at the point of initial condensation of vapour.
 - (e) In a shutdown situation where vapour containing chloride condenses and is re-evaporated when the unit is restarted.
 - (f) In a system where chloride can be continuously recycled, e.g. in a distillation process where there is recycle of a fraction of the distillate, chloride can concentrate in the still bottoms.
3. Maintaining the chloride-containing liquid in contact with the stainless steel at <70°C. Process design considerations limit this approach.
4. Using an alloy of higher stress-corrosion cracking resistance or one which is immune. If their general corrosion resistance is adequate, ferritic steels may be used. Extra-low-interstitial-content ferritic stainless steels containing molybdenum are claimed to have corrosion resistance at least the equal of the 300 series steels and to be virtually immune from stress-corrosion cracking. Otherwise, duplex-structure ferritic-austenitic alloys (typically Fe-18Cr-5Ni) are now available, having superior resistance to chloride stress-corrosion cracking, although cracking of them has been experienced in more acidic chloride-containing media. Stainless steels containing 18% Cr, 18% Ni and 2-3% Si are also reported to have been successfully used where type 304 has cracked.⁶

Alloys of high nickel content also have improved chloride stress-corrosion cracking resistance and Incolloy 825 has replaced type 321 stainless steel for steam bellows on some plants. Occasionally cracking of the latter was experienced due to chloride-contaminated steam condensing in the convolutions on shut-down and being re-evaporated at start-up.

Titanium is immune to chloride induced stress-corrosion cracking but more expensive than type 300 series stainless steels.

Chloride stress-corrosion cracking under lagging on hot equipment is a classic problem. Rainwater leaches chlorides from the lagging, the solution percolating to the hot wall of the vessel or pipe where it concentrates by evaporation. Several remedies are available. Wrapping the pipe or vessel with aluminium foil before lagging has proved effective. The chloride solution thus concentrates on the aluminium surface instead of stainless steel. Pipe hangers and vessel flanges constitute points where this protection can be incomplete and attention to detail is essential to minimise failures. Alternatively, lagging materials containing soluble inhibitors of chloride stress-corrosion cracking have been used with success.

For carbon steels, however, a full stress-relief heat treatment (580–620°C) has proved effective against stress-corrosion cracking by nitrates, caustic solutions, anhydrous ammonia, cyanides and carbonate solutions containing arsenite. For nitrates, even a low-temperature anneal at 350°C is effective, while for carbonate solution containing arsenite the stress-relief conditions have to be closely controlled for it to be effective⁵.

However, with large vessels, there are two areas where it is difficult to ensure adequate stress relief:

- (a) Where welds are stress relieved on site—the large heat sink provided by the vessel and the difficulty of shielding the area being heat treated from draughts mean that very strict temperature monitoring is necessary.
- (b) Vessels fitted with large branches—during pressure testing or even in normal operation, yield-point stresses can be reached at stress raisers provided by the configuration of such branches.

In addition, a surprisingly large number of stress-corrosion cracking failures have resulted from the welding of small attachments to vessels and piping after stress-relief heat treatment has been carried out.

Pitting (Sections 1.5 and 1.6) Pitting of carbon steel is seldom catastrophically rapid in service and can often be accommodated within the corrosion allowance for the equipment. It often takes place under scale or deposits so that regular descaling of equipment can be beneficial.

Pitting of carbon steel in cooling-water systems is a well-known problem which can be avoided by a correctly instituted and maintained inhibitor treatment. Correct institution includes descaling of the equipment before commissioning, since experience with chromate-inhibited systems has shown that a pre-existing rust layer prevents chromate reaching the metal surface, the equipment continuing to corrode as if no inhibitor was present in the cooling water.

'Oxygen pitting' of boiler tubes by boiler feed water due to inadequate de-aeration is also a problem, but controllable by proper maintenance of de-aerators, coupled with regular boiler feed water analysis, or, preferably, continuous dissolved-oxygen monitoring.

Pitting of stainless steels can usually be avoided by correct specification of steel type, and type 316 is the normal choice where pitting is at all likely.

Some duplex alloys have even better pitting resistance than type 316 and should be considered in severely pitting media. Titanium is virtually immune to chloride pitting and cupro-nickel alloys are used for condensers where sea-water is the coolant; high pitting resistance in this duty is claimed for Cu-25Ni-20Cr-4.5Mo.

Crevice corrosion without heat transfer (Sections 1.5 and 1.6) Since this is a phenomenon affecting alloys which depend on diffusion of an oxidising agent (usually oxygen) to the metal surface for maintenance of passivity, there are two degrees of freedom open to the designer to avoid this problem. The first is to choose an alloy that does not rely on an oxide film for its corrosion resistance. This, in the case of replacing conventional austenitic stainless steel, will be a more costly option. An alternative is to choose a passive alloy whose passivity is less critical in terms of oxidising agent replenishment at the metal surface. As an improvement on type 316, duplex-structure stainless steels, e.g. Ferralium or higher-alloy-content stainless steels based on a 25% Cr-20% Ni composition (e.g. 2RK65 and 904L) are more crevice-corrosion resistant, in addition to having improved general corrosion and stress-corrosion cracking resistance.

The second degree of freedom is 'to design-out' crevices where possible, although it must be remembered that crevice corrosion can go on underneath deposits. Crevice corrosion at a butt weld with incomplete root penetration is a common case (Fig. 9.7a). Where internal inspection is not possible and crevice corrosion is recognised as likely, X-radiography of each weld can be specified.

The correct flange design, in particular where crevice corrosion is known to be a problem, is important. Thus screwed flanges (Fig. 9.7b) and socket-welding flanges (Fig. 9.7c) present crevices to the fluid whereas slip-on-welding (Fig. 9.7d) and welding-neck flanges (Fig. 9.7e) are designs that avoid crevices. Welding-neck flanges have the advantage that the butt weld to the adjoining pipe can be radiographed whereas the fillet welds in the slip-on welding type cannot. Poor fusion resulting in a crevice cannot therefore be detected.

Crevice corrosion often occurs at gasketed joints. It can be alleviated as a problem by painting the flange faces with inhibited paints or coating the gasket and flange faces with impervious compounds, e.g. liquid rubbers, ensuring the gaskets are specified correctly from the design code and have the correct internal diameter. Figure 9.7f shows how a crevice is created when a gasket of a sub-standard specification (or the wrong size) is fitted. Figure 9.7g shows the correct configuration if crevice corrosion is thought likely. Branches for thermosheaths must be generously sized so that a crevice is not created between the sheath and the branch wall (Fig. 9.7h).

Crevice corrosion with heat transfer This can give rise to catastrophically high rates of corrosion. A classic situation in which this occurs is at the crevice formed at the back of a tubeplate in a tube-and-shell heat exchanger (Fig. 9.7i).

A heat-exchanger tube is expanded into the tubeplate to effect a joint. However, to avoid bulging the tube outside the confines of the tubeplate, expansion never takes place through the whole tubeplate thickness and a

crevice is thus formed. Within this crevice local boiling can take place, concentrating corrodents (chloride stress-corrosion cracking of austenitic-stainless-steel exchangers can occur in this way). Even if local boiling does not take place, the high rate of heat transfer across the gas entry tubeplate of a gas/liquid exchanger with gas on the tubeside, may by itself stimulate corrosion in the crevice. Where the shellside liquid is inhibited, ingress of inhibitor into the tube/tubeplate crevice may be too slow to be effective in a heat transfer situation.

There are three degrees of freedom in designing-out these problems for tube and shell exchangers:

1. By reducing the heat-transfer rate at the front tubeplate using insulating ferrules in the tube ends.
2. By putting the corrodent on the tubeside and the hot vapour on the shellside provided the vapour is compatible with the shell material; this is the normal configuration for steam-heated exchangers.
3. By eliminating the crevice using the recently developed technique of seal welding the tubes to the back of the tubeplate (Fig. 9.7k). However, this would add markedly to the cost of the unit.

Weld corrosion (Section 9.5) Crevice corrosion at butt welds due to poor penetration has already been discussed and was shown in Fig. 9.7(a). Conversely, if there is a large weld bead protruding in the pipe bore, erosion/corrosion can occur downstream due to the turbulence produced over the weld bead (Fig. 9.8). In either case, the fault probably lies in the incorrect spacing of the butts at welding.

Selective corrosion in the heat-affected zone of a weld occurs most commonly when unstabilised stainless steels are used in certain environments. The obvious answer is to use an extra-low-carbon grade of stainless steel, e.g. types 304L, 316L or a stabilised grade of steel, e.g. types 321 and 347. Knifeline attack at the edge of a weld is not commonly encountered and is seldom predictable, and it must be hoped that it is revealed during preliminary corrosion testing.

For both heat-affected zone corrosion (intergranular attack) and knifeline attack the heat flux during welding and the time at temperature can critically affect the severity of the attack. Both these factors may vary from one welder to another, and when preparing pieces for corrosion testing not only should fabrication welding conditions be accurately reproduced, but the work of more than one welder should be evaluated.

Erosion corrosion (Section 1.11) Erosion corrosion by a single-phase liquid system is characterised by a maximum acceptable fluid velocity for a given material. Generally, velocities in straight pipes should not exceed 50% of this value because turbulence, i.e. high local velocities, is bound to be superimposed in some areas. However, where possible, sharp changes in section and of flow direction should be avoided. Bends should be swept rather than right-angled, 'T'-junctions should be avoided where possible, and section reducers should be gradually tapered. Where turbulence cannot be avoided, e.g. downstream of pumps, control valves and orifice plates used to measure flow, it is advisable to consider short sections (say 3 m) of a more erosion-resistant material. Any piece of equipment in which turbulence

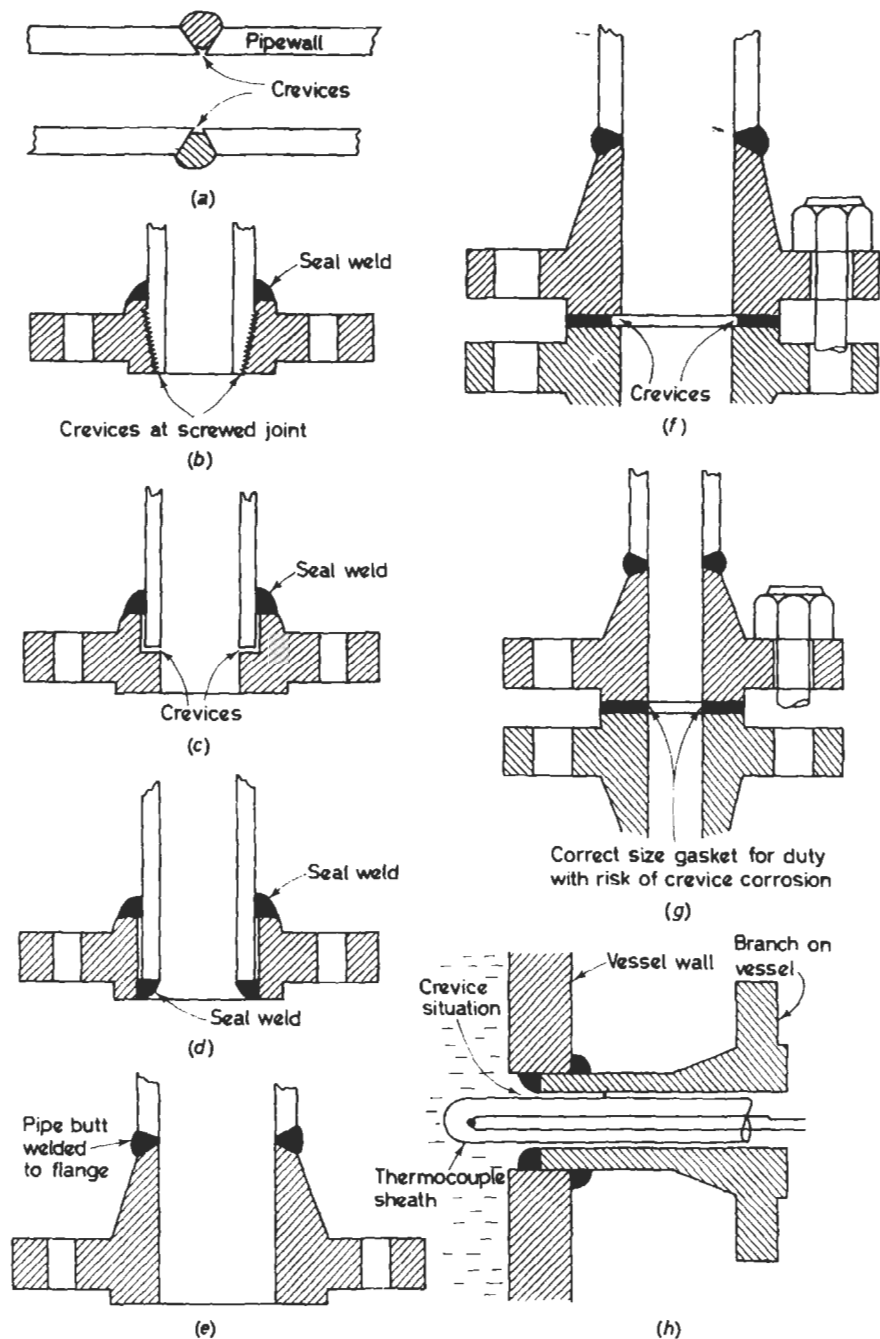
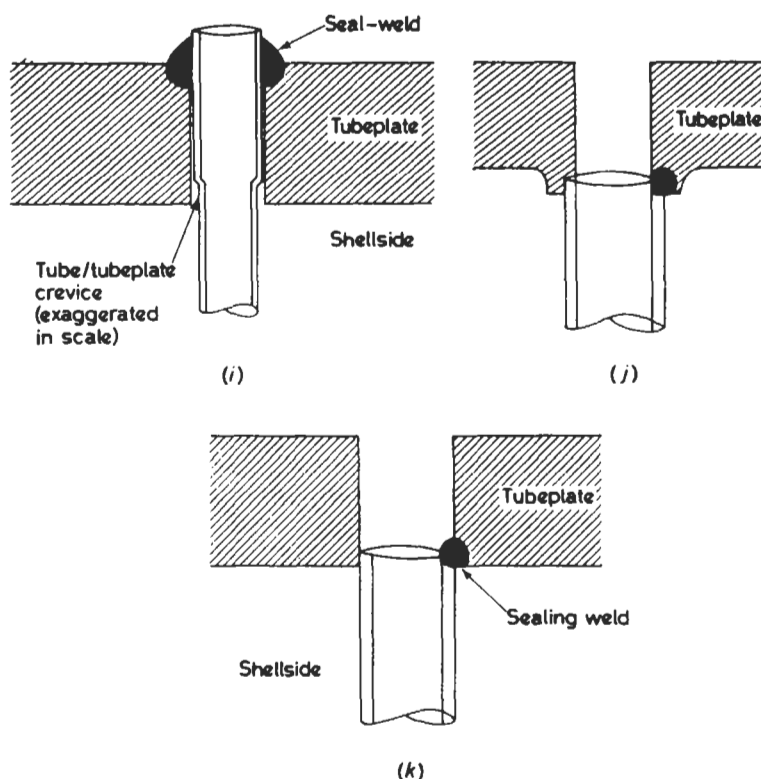


Fig. 9.7 Crevices. Formed (a) by the incomplete penetration of a butt weld. (b) by the use of a screwed flange and (c) by the use of a socket-welding flange. (d) Crevice-free slip-on-welding flange type, (e) crevice-free welding-neck flange type, (f) crevices created by choice of wrong size or wrong standard gasket for duty, (g) correct configuration if crevice corrosion is thought likely, (h) crevice situation created by too small a clearance between thermocouple sheath and the containing branch, (i) crevice formed at the back of a tubeplate and (j) and (k) variants of sealing the tube/tubeplate crevice



occurs, e.g. pumps and control valves, should similarly use a higher velocity-rating material of construction. Introduction of a sacrificial impingement plate should be considered when the velocity cannot be kept low enough to prevent erosion. For example, an impingement plate is often fitted opposite the liquid inlet on the shell of a tube-and-shell exchanger to protect the tubes on which the liquid would otherwise impinge.

The tube-side inlet to an exchanger, i.e. the tube ends, is a highly turbulent region and nylon ferrules in the tube ends of the inlet pass have been used in cupro-nickel-tubed condensers to prevent erosion. Where the flow is two phase the same rules will apply except that an erosion velocity limit is more difficult to specify.

Erosion corrosion of pump impellers, casings and wear plates can be very troublesome. Positive-displacement pumps create much less turbulence than centrifugal or axial-flow pumps and should be used where possible in critical



Fig. 9.8 Erosion/corrosion downstream of a butt weld with too much root penetration

duties where erosion is particularly severe or where the tolerable deviation from the design delivery rate is low. However, positive-displacement pumps tend to have low delivery rates, and for large rates pumps creating more turbulence will have to be used. For very severe duties, planned maintenance may be the only way to live with the problem. Experience on severe duties is that closed-impeller centrifugal pumps are less prone to erosion than the open type. Replaceable liners may also be considered to accommodate casing erosion.

Corrosion Data

This is derived from four sources:

1. From similar or identical plants – such data must be treated with caution until it is verified that process conditions, mode of operation and raw materials are all such that direct comparisons can be made.
2. From data published by manufacturers to support the use of their materials, e.g. References 7 to 10. Again, case histories quoted must be treated with caution but such data are very useful for sorting out the possible materials for a particular duty.
3. From established corrosion design data. There are some very useful reference works containing corrosion data from a multitude of sources¹¹⁻¹³, and for simpler corrosive systems, well-established corrosion design charts^{1,13}, e.g. limiting concentrations and temperatures above which carbon steel must be stress relieved to avoid stress-corrosion cracking in caustic solutions. These are invaluable to the corrosion engineer involved in design.
4. Corrosion testing data. The pitfalls in corrosion testing and the test methods are described in Chapter 19, but several points need underlining from experience in the design of chemical plants:
 - (a) Liquids used for testing must reproduce all possible variations that are to be expected in the operating plant.
 - (b) When testing for corrosion under heat-transfer conditions, the heat flux must be realistic. It is not good enough to merely reproduce the correct temperatures¹⁴.
 - (c) When testing for corrosion in a distillation process, very localised effects must be covered, e.g. the corrosion characteristics at the point of initial condensation of the overhead vapours.
 - (d) Testing for erosion limits should include a reference condition, i.e. a fluid velocity/material combination whose erosive characteristics in a plant are known.

New Materials and Equipment Design

New alloys with improved corrosion-resistance characteristics are continually being marketed, and are aimed at solving a particular problem, e.g. improved stress-corrosion cracking resistance in the case of stainless steels improved pitting resistance or less susceptibility to welding difficulties.

Composite materials are also becoming more freely available and explosive cladding offers possibilities of duplex-plate materials for such items as tubeplates¹⁵. Duplex-material heat-exchanger tubing is also now marketed and vessels can be satisfactorily clad or lined with an ever increasing list of metallic and non-metallic linings. Glass-reinforced plastics are in increasing use as confidence grows in their long-term performance for such items as low-pressure vessels. In short, the impasse of a design today may well be soluble tomorrow and the materials engineer must keep abreast of developments.

Economic and Political Considerations

This input to design refers to the long-term stability of the raw material sources for the plant. It is only of importance where the raw materials can or do contain impurities which can have profound effects on the corrosivity of the process. Just as the design should cater not only for the norm of operation but for the extremes, so it is pertinent to question the assumptions made about raw material purity. Crude oil (where H₂S, mercaptan sulphur and naphthenic acid contents determine the corrosivity of the distillation process) and phosphate rock (chloride, silica and fluoride determine the corrosivity of phosphoric acid) are very pertinent examples. Thus, crude-oil units intended to process low-sulphur 'crudes', and therefore designed on a basis of carbon-steel equipment, experience serious corrosion problems when only higher sulphur 'crudes' are economically available and must be processed.

Phase Two — Construction Stage Checks

The question of safeguarding against wrong materials being installed in a plant has been a focus of much attention recently¹⁶. Mistakes can arise in two ways:

1. Items which cannot themselves be wrongly assembled are supplied in the wrong material by the fabricator due to a mix-up in his identification system.
2. Common items such as valves, piping and welding electrodes which may be supplied for a large plant in half a dozen material specifications can become mixed up due to poor identification marking.

This is a very serious problem in that, for example, in high-temperature hydrogen service, use of carbon steel when the duty demands a 1% Cr-Mo steel, can have disastrous consequences¹⁶.

Corrosion failures in service are minimised by ensuring that all fabrication and erection work conforms to the codes of practice specified by the design. The corrosion engineer can only influence matters here by persuading the designers to specify more stringent codes if there are identifiable risks in using a less demanding code. For example, for duties in which crevice corrosion is a possible problem, it might pay to adopt a policy of radiographing all welds for defects rather than only 10% as specified normally.

Phase Three — Planned Maintenance

Strictly, 'planned maintenance' refers to a policy of shutting down a plant at regular intervals to replace or refurbish items of equipment which although not having failed by corrosion or any other mode, would have a high probability of doing so before the next shutdown.

The justifications for adopting a planned maintenance policy rather than spending extra capital to ensure that the component lasts the life of the plant are summarised in Fig. 9.9.

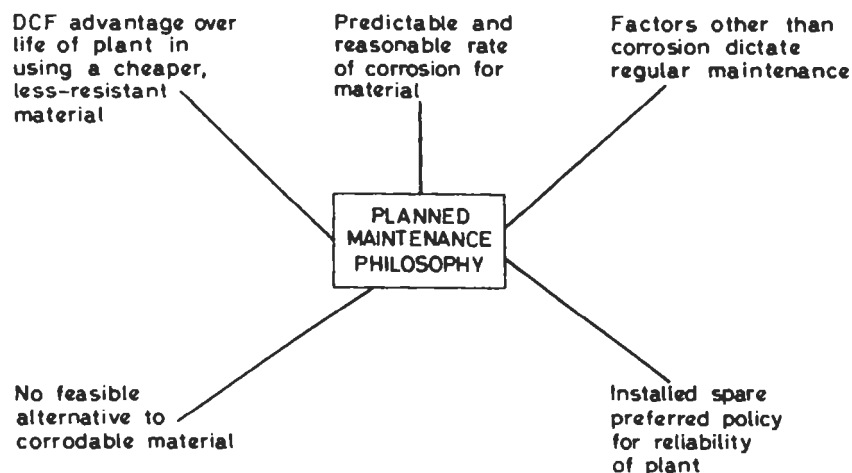


Fig. 9.9 Factors contributing to a policy of planned maintenance

A prerequisite to a corrodable material being used is that it is known to have a useful and reasonably predictable life. Planned, or unplanned downtime costs money and the intervals between planned replacements must be of reasonable duration. In practice, the replacement interval is usually conservative at first and then as experience accumulates, the intervals between planned replacements will usually extend. The main reason for choosing a planned maintenance policy is that on a discounted cash flow (DCF) calculation over the life of the plant, the cost of regular replacements including maintenance labour and downtime is less than the extra initial capital cost of a more durable material.

In some cases, the item of equipment may have to undergo maintenance at regular intervals for reasons other than corrosion damage, e.g. change of bearings and seals on pumps. This fact alters the basis of the DCF calculation, i.e. the cost of downtime and maintenance labour is no longer all set against the increased cost of a more durable material and the cheaper, corrodable material becomes a more attractive alternative. For some items of equipment, their importance to the plant may be such that the minimum risks of failure shutting the plant down are taken, and a spare, which can be rapidly brought on-line, is installed. In this case, maintenance can be carried out on the spare with the plant on-line. This is a variation on the strict definition of planned maintenance.

Lastly, but quite frequently, the sole justification for a planned maintenance policy is that there is no feasible alternative to the use of a corrodible material of construction, usually because the item of equipment in a non-corrodible material is not commercially available or delivery is slow such that the construction programme would be jeopardised.

Phase Four — Corrosion Monitoring

Figure 9.10 summarises the techniques available for monitoring corrosion in an operating plant. Visual inspection is a statutory obligation at regular intervals for some classes of chemical plant equipment, e.g. pressure vessels. However, much equipment is opened up mainly to gain reassurance that it is not suffering from serious corrosion damage. Due to the high cost of such downtime, there is a considerable financial incentive to develop on-line monitoring methods which will partially or wholly replace such visual inspections. (See also Section 19.3.)

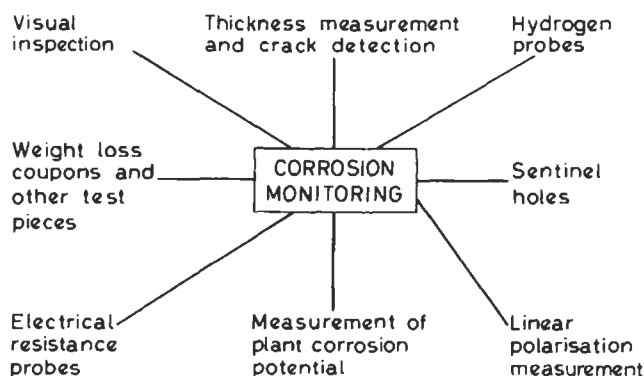


Fig. 9.10 Techniques for monitoring corrosion in process plant

Thickness Measurement and Crack Detection

The principal technique used is ultrasonics, but it has limitations as a monitor for the progress of corrosion. The sensitivity of the technique is commonly quoted as ± 0.005 in. (0.125 mm) although even this may be difficult to achieve where the surface is hot or where close coupling of the probe head and metal surface is difficult. This means that for a normally low corrosion rate, the useful interval between readings may be fairly long and an unexpected rapid increase in corrosion rate could be missed for some time.

γ -ray and β -ray backscatter and absorption techniques can give very accurate thickness definition, especially for thin gauge material. The γ -ray absorption method has been successfully developed to detect corrosion in the tube/tubeplate crevice of a heat exchanger and also of the shellside of heat-exchanger tubes¹⁸. Both situations are difficult to visually inspect. The

γ -source is placed in one tube while the detector is placed in an adjacent one.

For detecting stress-corrosion cracks and estimating their depth of penetration, the ultrasonic technique and, to a lesser extent, *X*-radiography, have proved successful.

Sentinel holes are used as a simple form of thickness testing. A small hole of about 1.6 mm diameter is drilled from the outer wall of the piece of equipment to within a distance from the inner wall (in contact with the corrodent) equal to the corrosion allowance on the equipment (Fig. 9.11). The technique has been used even in cases where the corrodent spontaneously ignites on contact with the atmosphere. The philosophy is that it is better to have a little fire than a big one which would follow a major leak from corrosion through the wall. When the sentinel hole begins to weep fluid a tapered plug is hammered into the hole and remedial maintenance planned. Siting the sentinel holes is somewhat speculative although erosion at the outside of a pipe bend is often monitored in this way.

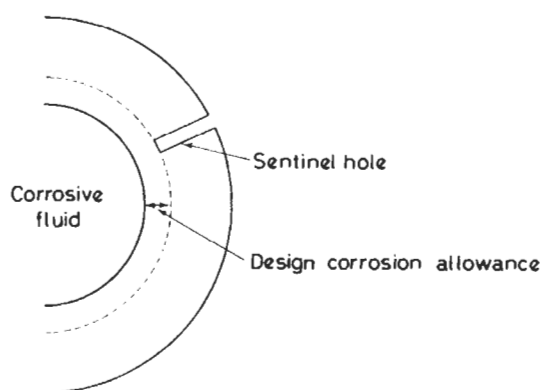


Fig. 9.11 Sentinel hole method of monitoring corrosion of a pipe wall

Hydrogen probes are mainly used in refineries to detect the onset of conditions when H_2S cracking of carbon-steel equipment could become a real risk. As a qualitative monitoring technique, it has a long and proven service of worth.

Weight-loss coupons are the most used and most abused of corrosion-monitoring methods. The technique is abused by the often repeated mistake of coupons being placed in such a position that the fluid flow around them is totally unrepresentative of that experienced by the equipment they are intended to simulate. The flow around a specimen projecting into a flowing piped stream may result in totally different corrosion conditions from that experienced by the pipe walls. A less precise result from a spool piece inserted into a pipeline may be far more typical of true corrosion rates in the pipe than a highly precise result from a corrosion coupon. Sometimes, however, it is possible to get close to actual flow conditions. Thus, in agitated vessels, specimens bolted to the outer edge of the agitator blade, in the same orientation as the blade, will give very useful information on agitator corrosion rates. Corrosion coupons are probably most usefully used to rank materials of construction and to detect the permanent onset of a significant change in

corrosivity. Coupons integrate corrosion damage over a period and are of only marginal use in a situation where rapid and large increases in corrosion rate can occur.

Electrical Resistance Monitors

Electrical resistance monitors use the fact that the resistance of a conductor varies inversely as its cross-sectional area. In principle, then, a wire or strip of the metal of interest is exposed to the corrodent and its resistance is measured at regular intervals. In practice, since the resistance also varies with temperature, the resistance of the exposed element is compared in a Wheatstone bridge circuit to that of a similar element which is protected from the corrodent but which experiences the same temperature.

In process streams where there are large changes in process temperature over a short time, the fact that the temperature of the protected element will lag behind that of the exposed element can give rise to considerable errors. The most recent development is the use of test and reference elements that are both exposed to the corrodent. The comparator element has a much larger area than the measuring element so that its resistance varies much less than that of the measuring element during their corrosion. Several drawbacks to this type of monitor, deduced from service experience, may be quoted:

1. If corrosion occurs with the formation of a conducting scale, e.g. FeS or Fe_3O_4 , then a value of the measured element resistance may be obtained which bears little relation to the loss in metal thickness.
2. Pitting or local thinning of the measured element effectively puts a high resistance in series with the rest of the element and thus gives a highly inflated corrosion rate.
3. Wire form measured elements tends to suffer corrosion fatigue close to the points where it enters the support. This is particularly true in turbulent-flow conditions, and strip-type elements are preferred in such cases.
4. Where a solid corrosion product is formed, meaningful results are only obtained after a 'conditioning' period for a new measured element. Even so, the conditions under which the scale is laid down may not be the same as that for the original equipment. This objection applies equally to coupons or spools, and points to one of the basic objections of using anything other than the plant itself to monitor corrosion rates.
5. The more massive the measured element, the longer its useful life, but the less sensitive the monitor is to small changes in cross-sectional area. Thus, a compromise between long life and sensitivity has to be decided upon, depending on the application.

The advantages of this type of monitor are that it can be automated to produce print-outs of corrosion rate at regular intervals and that it can be used to monitor corrosion in any type of corrodent, e.g. gaseous, non-ionic liquid or ionic electrolyte. Such monitors are in wide use, especially in refinery applications.

Linear Polarisation Measurement

Linear polarisation measurement is based on the Stern-Geary equation:

$$\left(\frac{\Delta E}{\Delta i}\right)_{E_{\text{corr}}} = -\frac{b_a b_c}{2 \cdot 3 i_{\text{corr.}} (b_a + b_c)}$$

$$i_{\text{corr.}} = K \left(\frac{\Delta i}{\Delta E}\right)$$

There has been considerable talk recently in the literature about errors in this equation, but the modifications to it proposed are minor compared with the practical errors introduced by its use (see also Section 19.1):

1. The values of b_a and b_c , i.e. The Tafel constants of the anodic and cathodic polarisation curves, first have to be measured directly in the laboratory or deduced by correlating values of $\Delta E/\Delta i$ measured on the plant with $i_{\text{corr.}}$ values deduced from corrosion coupons. The criticism is that the K value is likely to be inaccurate and/or to change markedly as conditions in the process stream change, i.e. the introduction of an impurity into a process stream could not only alter $i_{\text{corr.}}$ but also the K factor which is used to calculate it.
2. The equation assumes that for a given ΔE (usually 10 mV) shift, the corresponding change Δi is solely attributable to an increase in metal dissolution current. However, in solutions containing high redox systems, this may be very far from the case.

Practical experience with the technique has been that in some simple electrolyte solutions, 'reasonably good' correlation is achieved between corrosion rates deduced by linear polarisation and from corrosion coupons. 'Reasonably good' here seems to be considered anything better than a factor of two or three. However, the a.c. linear-polarisation technique has been used with considerable success to control inhibitor additions to overcome corrosion in ships' condensers while operating in estuarine waters¹⁸ and the d.c. technique has been used in controlling the corrosivity of cooling waters. Although it can only be used in ionic electrolyte solutions, results have indicated that the necessary conductivity is not as high as was once thought to be the case.

To summarise: the technique is very much in its infancy as a monitoring method and must be used with caution until proven in specific applications.

Corrosion Potential Measurement

The application of this method of corrosion monitoring demands some knowledge of the electrochemistry of the material of construction in the corrodent. Further, it is only applicable in electrolyte solutions.

The nature of the reference electrode used depends largely on the accuracy required of the potential measurement. In the case of breakdown of passivity of stainless steels the absolute value of potential is of little interest. The requirement is to detect a change of at least 200 mV as the steel changes from

the passive to the active state. In this case a wire reference electrode, e.g. silver if there are chloride ions in solution to give a crude reversible silver/silver chloride electrode, may well be sufficient. Alternatively, the redox potential of the solution may be steady enough to be used as a reference potential by inserting a platinum wire in the solution as the wire electrode.

However, in the case of stress-corrosion cracking of mild steel in some solutions, the potential band within which cracking occurs can be very narrow and an accurately known reference potential is required. A reference half cell of the calomel or mercury/mercurous sulphate type is therefore used with a liquid/liquid junction to separate the half-cell support electrolyte from the process fluid. The connections from the plant equipment and reference electrode are made to an impedance converter which ensures that only tiny currents flow in the circuit, thus causing the minimum polarisation of the reference electrode. The signal is then amplified and displayed on a digital voltmeter or recorder.

Corrosion potential measurement is increasing as a plant monitoring device. It has the very big advantage that the plant itself is monitored rather than any introduced material. Some examples of its uses are:

1. To protect stainless-steel equipment from chloride stress-corrosion cracking by triggering an anodic protection system when the measured potential falls to a value close to that known to correspond to stress-corroding conditions.
2. To trigger off an anodic protection system for stainless-steel coolers cooling hot concentrated sulphuric acid when the potential moves towards that of active corrosion.
3. To prompt inhibitor addition to a gas scrubbing system solution prone to cause stress-corrosion cracking of carbon steel when the potential moves towards a value at which stress-corrosion cracking is known to occur.
4. To prompt remedial action when stainless-steel agitators in a phosphoric-acid-plant reactor show a potential shift towards a value associated with active corrosion due to an increase in corrosive impurities in the phosphate rock.

It can be seen that in each case considerable knowledge is required before the potential values associated with the equipment can be interpreted.

Monitor Retractability

Corrosion coupons require periodic weighing, resistance-probe elements require renewing and reference electrodes develop faults. Since the emphasis is on monitoring plants which remain on-line for long periods, careful consideration has to be given to how the monitor is going to be serviced. Systems are now marketed which enable such servicing to be carried out with the plant on-line and these do not rely on the monitoring being installed in a by-pass line or in line with a duplicated piece of equipment such as a pump, which may not always be in use. Figure 9.12 shows a system based on a tool used for under-pressure break-in to operating plant.

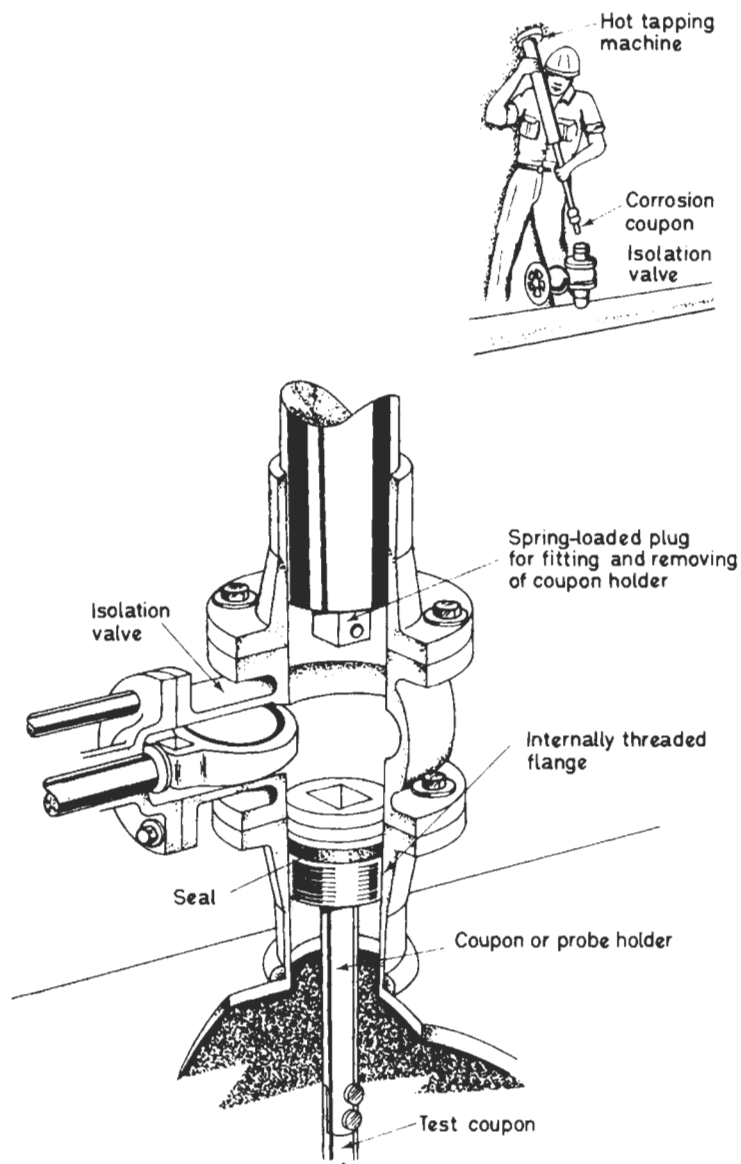


Fig. 9.12 System based on a tool used for under-pressure break-in to operating plant

Phase Five — Remedial Measures

Figure 9.13 summarises the tools which are at the corrosion engineer's disposal in the solution of a corrosion problem once it has appeared. The solution adopted will frequently be a combination of these, and economics and convenience will determine the course adopted if there is an option.

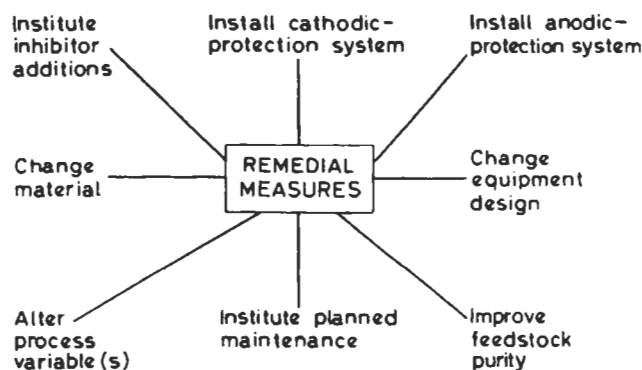


Fig. 9.13 Options for remedying corrosion problems in process plant

Summary

Corrosion control in chemical plant is a continuous effort from the inception of the design to the closure of the plant. Economics dictate the risks which are taken at the design stage with respect to corrosion and the extent of the precautions taken to prevent it.

Errors in design and changes in operation will occur which increase the risk of corrosion. Corrosion-monitoring systems give advance warning and enable remedial measures to be worked out and adopted.

Recent Developments

Introduction

The format of the original section has been adopted in this update. Because of the 'timeless' nature of the original material relating to phases 2 and 3, updating has been confined to phases 1, 4 and 5.

Phase One — Plant and Process Design

Information/Knowledge Systems Computers have revolutionised the basic process/mechanical design processes, and are beginning to impact significantly on the corrosion engineer's role of predicting material performance¹⁹. Apart from the increasing availability of computerised databases, significant effort is being expended on the development of computer-aided management and expert systems. There has been much debate around desirable and practicable objectives for such systems²⁰, but most are directed at one or more of the basic elements of education, failure diagnosis and materials selection.

The development of such systems is expensive and time consuming, and the major industrial initiatives have been undertaken on a collaborative

basis. Of particular note are the UK ACHILLES²¹, the European PRIME²² and the North American Materials Technology Institute (MTI), National Association of Corrosion Engineers (NACE) and National Institute for Standards and Technology (NIST) projects which when complete will provide expert systems relating to a wide range of process industry environments and corrosion control technologies.

Major Industry Corrosion Problems A number of specific problems have achieved 'industry' status over the past ten years, owing to their cost and/or threat to plant integrity. All have significant design implications.

1. 'External' corrosion of surfaces beneath thermal insulation and fireproofing systems, resulting in general corrosion of carbon and low-alloy steel, and chloride-induced stress-corrosion cracking of austenitic stainless steel. Key preventative measures are to keep water out of such systems, to allow it to be removed should it get in, the specification of appropriate insulating/fireproofing materials, and the use of protective coatings²³.
2. The effects of hydrogen on carbon and low-alloy steel equipment:
 - (a) It has become recognised that 0.5 C-Mo grades of steel can suffer more hydrogen 'damage' at elevated temperatures than indicated by the API 'Nelson' curves, the most recent edition of which draws attention to the problem²⁴.
 - (b) The various forms of 'wet H₂S' cracking and blistering, familiar in the oil and gas production industry, have been experienced in storage and pressure vessels in the refining industry²⁵, and have contributed to at least one major failure²⁶. Preventive measures similar to those utilised in oil and gas production, including hardness control and stress relief²⁷, are necessary to avoid cracking.
3. Environmentally-induced cracking has emerged as a significant problem in the following fluids:
 - (a) Anhydrous ammonia. This potential problem is now widely recognised in ammonia storage/processing equipment²⁸. Oxygen and water promote and inhibit cracking, respectively. The problem has been heavily researched on an 'industry' basis in Europe²⁹, and key factors for controlling the problem recognised.
 - (b) Amine-based acid gas removal systems. Cracking can occur in both CO₂ and H₂S removal units utilising MEA, DEA, MDEA and DIPA, and has been reported in all types of equipment, including absorbers/contactors, exchangers and piping. An industry survey has been undertaken³⁰.
 - (c) 'Deaerated' water. Following some problems in the pulp/paper industry, it is now clear that process and utility industry deaerated water storage vessels, and possibly other steam/water circuit equipment, can suffer environmentally induced cracking³¹. The origins of the problem remain rather obscure, but there are probable parallels to the well understood nuclear pressure vessel cracking problems, where critical levels of oxygen promote cracking³².

The evidence to date suggests that thermal stress relief prevents cracking in all three environments.

Phase Four — Corrosion Monitoring

A number of techniques have been developed since the original material was written³³. Some instrumentation/transducer developments also merit comment.

Electrochemical Techniques Although the linear polarisation resistance technique has moved beyond the 'infancy' status attributed to it in the original material, its inherent limitations remain, i.e. it is a perturbation technique, sensitive to environmental conductivity and insensitive to localised corrosion. Two developments have occurred:

1. A.c. impedance. Measurements of the frequency variation of impedance^{33,34} allow separation of the 'charge transfer resistance' from the contributions to the total impedance of the environment resistance, surface films, adsorbed layers, etc. Robust instruments utilising a two-frequency technique have been developed^{35,36}.
2. Electrochemical noise. Fluctuations in potential or current from baseline values during electrochemical measurements are particularly prominent during active/passive transitions. This so-called 'electrochemical' noise is of particular value in monitoring localised corrosion, i.e. pitting, crevice and deposit corrosion and stress-corrosion cracking^{36,39}.

Instruments providing simultaneous measurement of a number of parameters on multi-element probes have been developed, including potential 'noise', galvanic coupling, potential monitoring, and a.c. impedance³⁸.

Reported plant applications of a.c. impedance and electrochemical noise are rare, but include stainless steels in terephthalic acid (TA) plant oxidation liquors³⁵, nuclear fuel reprocessing³⁷, and fluegas desulphurisation (FGD) scrubber systems³⁸.

Radioactivation Techniques Neutron and thin layer (TLA) activation are non-intrusive techniques offering the prospect of continuous, direct component monitoring, in addition to coupon or probe, monitoring. In principle, localised corrosion can be monitored using a double-layer technique. Process plant applications of the technique have been limited to date⁴⁰.

Acoustic Emission (AE) Conventional, periodic internal inspection of process equipment is highly expensive, particularly where an in-service deterioration mechanism, e.g. stress-corrosion cracking or corrosion fatigue is suspected. The potential for AE as a basis for plant integrity monitoring has been recognised over the past 10 years⁴¹. Monsanto have been particularly active in extending technology developed initially for fibre reinforced plastic (FRP) equipment to the assessment of metallic equipment⁴².

The technique utilises arrays of transducers attached to the external surfaces of the equipment, which detect small-amplitude elastic stress waves emitted when defects 'propagate'. Using sophisticated computational techniques, 'events' can be characterised in terms of their severity and location.

Conventionally, the technique has been used off-line, to provide information on the structural integrity of equipment, typically during a pressure test. However, the technique can be used on line by periodically raising the pressure some 5–10% above the maximum operating pressure and one system

for the continuous monitoring of stress corrosion cracking in blast furnace plants has been described⁴³.

Complementary technologies such as conventional non-destructive examination (NDE) and fracture mechanics are needed to size and determine the significance of defects revealed by AE.

Probe/Instrumentation Developments The principles of good practice in the design, construction and location of corrosion probes have been reviewed⁴⁴. Specific probe designs which acknowledge hydrodynamic influences⁴⁵ and the combined effects of mass and heat transfer³⁸ have been developed.

Computers have impacted significantly on corrosion monitoring instrumentation and data management⁴⁶. Cableless corrosion monitoring utilising radio techniques has recently become available⁴⁷.

Phase Five – Remedial Measures

Significant developments have occurred in many of the basic corrosion prevention technologies over the past 10 years.

Metallic Materials Stainless steel technology has been revolutionised by the combined effects of argon oxygen decarburisation (AOD) and nitrogen alloying (0.1–0.25%) producing a range of alloys with improved localised corrosion (including chloride stress corrosion) resistance, and in specific cases oxidising or reducing acid resistance, compared with the basic 18Cr–8Ni grades⁴⁸.

The principal groups are:

1. Ferritic Fe–Cr–Mo compositions with 18–30% Cr, 1–4% Mo and in some cases up to 4% Ni.
2. Duplex ferritic–austenitic alloys with 18–26% Cr, 5–7% Ni and up to 4% Mo.
3. High nickel austenitics, with 25–35% Ni, 20–22% Cr and up to 6% Mo, with good resistance to reducing acids.
4. High chromium austenitics with 24–25% Cr, 20–22% Ni and up to 2% Mo, with good nitric acid resistance.
5. High silicon austenitics, containing 4–6% Si, with good resistance to highly oxidising nitric and sulphuric acids.

Nickel alloy technology has also been influenced by AOD melt processing, allowing the production of more weldable variants of the basic 'B', 'C' and 'G' families of alloys. Additional improvements have come from alloying around the basic Ni–Mo and Ni–Cr–Mo compositions⁴⁹.

Non-Metallic Materials Numerous engineering thermoplastics have been commercialised⁵⁰ including materials such as polyetherether ketone (PEEK) and polyether sulphate (PES) with much improved thermal/chemical resistance. The usage of FRP equipment has increased, and fluoropolymer lining technology/applications have come of age. Of particular interest is the development of stoved, fluoropolymer coating systems for process industry equipment.

Electrochemical Protection Potential control technology has developed considerably in recent years beyond the more traditional applications in sulphuric acid storage, cooling etc. Numerous applications have been identified in the pulp and paper industry, including the control of stress-corrosion cracking, pitting and crevice corrosion³¹. Systems have also been developed for plate heat exchangers, FGD scrubbers, and phosphoric acid storage vessels.

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9.3 Design for Prevention of Corrosion in Buildings and Structures

The prevention of corrosion must begin at the design stage, and full advantage should be taken of the range of protective coatings and corrosion-resistant materials available. Furthermore, at this stage particular attention should be paid to the avoidance of geometrical details that may promote or interfere with the application of protective coatings and their subsequent maintenance. Consideration should also be given to the materials to be used, the methods of protection, fabrication and assembly, and the conditions of service.

The corrosion of metal components in buildings may have important and far-reaching effects, since:

1. The structural soundness of the component may be affected.
2. Where the component is wholly or partly embedded in other building materials, the growth of corrosion products on the face of the metal may cause distortion or cracking of these materials; trouble may also arise when the metal is in contact with, although not embedded in, other building materials.
3. Failure of the component may lead to entry of water into the building.
4. Unsightly surfaces may be produced.
5. Stresses produced in the metal during manufacture or application may lead to stress-corrosion cracking.

The Corrosive Environment

The conditions to which a metal may be exposed can vary widely¹, but broadly the following types of exposure may arise.

Exposure to external atmospheres The rate of corrosion will depend mainly on the type of metal or alloy, rainfall, temperature, degree of atmospheric pollution, and the angle and extent of exposure to the prevailing wind and rain.

Exposure to internal atmospheres Internal atmospheres in buildings can vary; exposure in the occasionally hot, steamy atmosphere of a kitchen or bathroom is more severe than in other rooms. Condensation may occur in

roof spaces or cavity walls. One particularly corrosive atmosphere created within a building and having its effect on flue terminals is that of the flue gases and smoke from the combustion of various types of fuel.

Embedment in, or contact with, various building materials Metal components may be embedded in various building mortars, plasters, concrete or floor compositions, or else may be in contact with these. Similarly, they may be in contact with materials such as other metals, wood, etc.

Contact with water or with water containing dissolved acids, alkalis or salts Many details in building construction may permit rain water to enter and this may be retained in crevices in metal surfaces, or between a metallic and some other surface. Water may drip on to metal surfaces. These conditions, which can involve a greater risk of corrosion than exists where a metal is exposed to the normal action of the weather, are more severe when the water contains dissolved acids, alkalis or salts derived from the atmosphere or from materials with which the water comes into contact. Normal supply waters can also cause corrosion.

Contact between dissimilar metals Galvanic action can occur between two different bare metals in contact if moisture is present, causing preferential corrosion of one of them (see Section 1.7).

It is thus important to consider all types of exposure. If a building is to be durable and of good appearance, special attention must be paid to the design of details, especially those involving metals, and precautions must be taken against corrosion, since failure which is not due to general exposure to the external atmosphere often occurs in components within or structurally part of the building.

Ferrous Metals

Faulty geometrical design is a major factor in the corrosion of ferrous metals. A design may be sound from the structural and aesthetic points of view, but if it incorporates features that tend to promote corrosion, then unnecessary maintenance costs will have to be met throughout the life of the article, or early failure may occur.

Some of the more important points that should be observed are noted below². Where these cannot be implemented, extra protection should be provided.

Air

1. Features should be arranged so that moisture and dirt are not trapped. Where this is not practicable consideration should be given to the provision of drainage holes of sufficient diameter, located so that all moisture is drained away (Fig. 9.14).

2. Crevices should be avoided. They allow moisture and dirt to collect with a resultant increase in corrosion. If crevices either cannot be avoided, or are present on an existing structure, they can often be filled by welding or by using a filler or mastic.

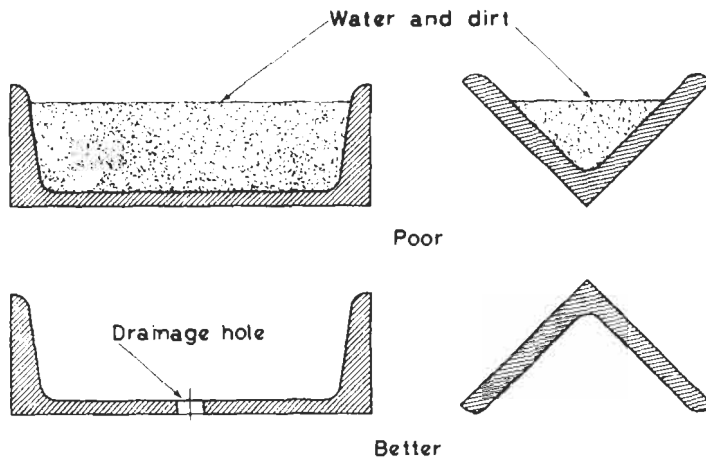


Fig. 9.14 Channels and angles

3. Joints and fastenings should be arranged to give clean uninterrupted lines. Welds are generally preferable to bolted joints, and butt welds to lap welds. If lap joints have to be used, then appropriate welding or filling may be necessary to avoid the entrapment of moisture and dirt (Fig. 9.15).

4. Condensation should be reduced by allowing free circulation of air, or by air-conditioning. Storage tanks should be raised from the ground to allow air circulation and access for maintenance and provision should be made for complete drainage (Fig. 9.16).

5. All members should either be placed so that access is provided for maintenance, or so thoroughly protected that no maintenance will be required for the life of the equipment or structure.

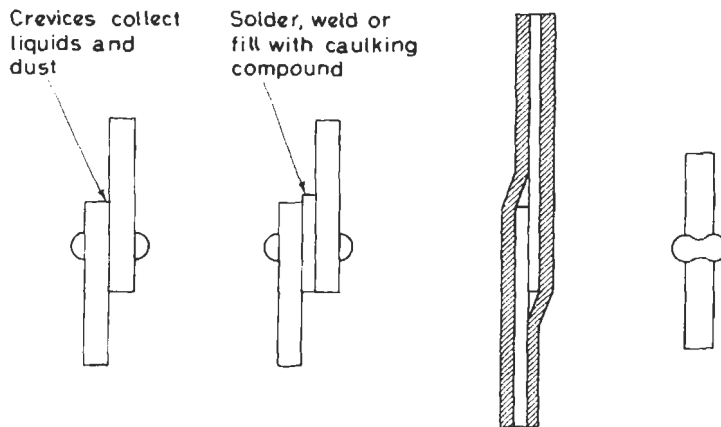


Fig. 9.15 Welded and riveted joints

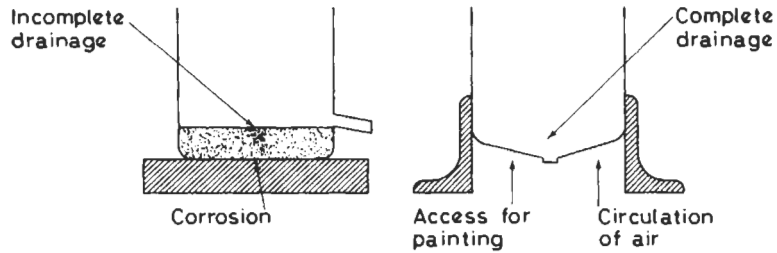


Fig. 9.16 Storage tanks

6. Where practicable, rounded contours and corners are preferable to angles, which are subject to mechanical damage at edges and are difficult to coat evenly¹. Tubular or rolled hollow sections could often advantageously replace 'I' or 'H'-sections (Fig. 9.17).

7. Corrosion is often particularly pronounced on sheltered surfaces where the evaporation of moisture is retarded. Design features of this kind should either be avoided or additional protection provided.

8. Steel should not be exposed to contact with water-absorbent materials and care must be exercised when using steel in contact with wood. Not only is wood absorbent, but the vapours from it may be corrosive in enclosed spaces.

9. Large box-section girders can be enclosed by welding-in bulkheads near the ends; the welds must not have gaps or condensation may occur within the box section.

10. Features that allow moisture to drip on to other parts of a structure should be avoided, and in this connection particular attention should be paid to the siting of drainage holes.

11. Where steel members protrude from concrete, or in similar situations, attention should be given to the position of abutment. This should be arranged so that water drains away from the steel.

12. When surfaces are being bolted, the holes should coincide and bolts

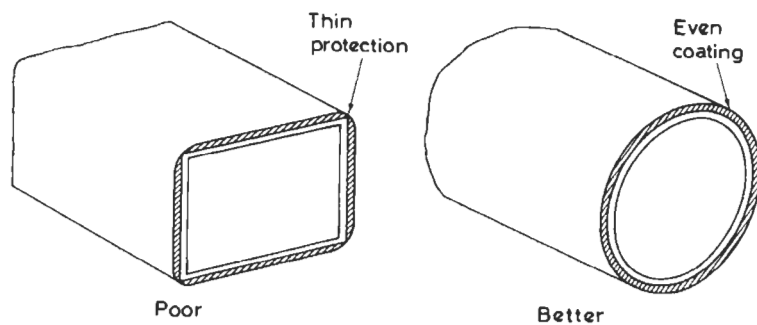


Fig. 9.17 Contour used in construction

must not be forced into undersize holes, since the resulting stresses may result in stress-corrosion failure.

13. The corrosion of painted mild-steel window frames is often troublesome, especially on horizontal members where moisture tends to collect. This effect can be reduced by bevelling the edges with putty before painting, to help drainage. It is preferable, however, to use more resistant materials such as galvanised steel, stainless steel or aluminium for window frames.

Materials of Construction

There are three broad categories of steel⁴:

1. Mild steels to which only small amounts of alloying elements are deliberately added, e.g. manganese (Section 3.1).
2. Low-alloy steels to which 1–2% of alloying elements are added (Section 3.2).
3. Highly alloyed steels, such as stainless steels, which contain 12–20% Cr and sometimes up to 10% Ni and 3% Mo (Section 3.3).

Mild Steels

Most steels fall into this category, ranging from large structural sections to thin sheet, and minor variations in composition do not markedly affect their corrosion resistance. This is not generally important since such steels are usually protected by some form of coating which is specific for the condition of service.

Account should be taken of this fact when planning to use this type of steel, so that the coating can be applied at the stage at which the maximum benefits will result. At the same time, thought should also be given to the type of coating and its method of application, since one geometrical design may be more suitable for one particular type of coating application than another.

The more automatic the method of coating application, the more economical and efficient it is, since automation lends itself more readily to more even coatings than do manual methods, e.g. large surface areas lend themselves more readily to spraying techniques, whereas open work structures are more suitable for dipping methods. The coating should also be applied to a specified minimum thickness which is adequate for the service conditions and life envisaged.

Surface preparation is of prime importance, and optimum performance of modern protection coatings can be achieved only if the surface of the steel has been adequately treated. The method of surface preparation depends on the shape and size of the structure or component. Thus it is preferable to blast-clean an openwork steel structure by manual methods, since with this type of structure automatic blast cleaning would lead to excessive impingement of the abrasive on the machine itself.

Steel, whether in structural form or as a sheet, can be protected by many different coating systems, such as paint, plastic materials, concrete and other metals, either singly or in combination (such as a metal coating followed by a paint system, or a plastic coating). Examples of this compound type of

protection are the new Forth road bridge and the Severn bridge, both of which are protected by sprayed metal plus a paint system. (See also Section 12.4.)

Low-alloy Steels

Low-alloy steels usually contain small percentages of alloying elements, such as copper, chromium and nickel, up to a total of 1–2%. Under favourable conditions they tend to corrode less rapidly than the ordinary carbon steels when exposed freely in air. Under sheltered conditions, or in crevices, they may well corrode at the same rate as mild steels⁵.

When such steels are exposed bare, the initial appearance of the rust is similar to that on mild steel, although in time it tends to become darker, more compact, and of a more even texture than ordinary rusts.

When low-alloy steels are considered for use in the bare condition, the remarks made earlier with regard to design must be given even greater attention, particularly in relation to crevices and sheltered areas. Also, the appearance and performance must be acceptable for the specific application, and care should be taken to ensure that adjacent concrete and stonework is not stained brown in the early stages by moisture dripping from the rusted steel. This can be accomplished by the following: attention to design, the careful siting of the rainwater drainage system, the use of loose gravel that can be raked over, painting the concrete or in several other ways.

Low-alloy steels can be obtained as structural sections or in sheet form, and must be blast-cleaned to remove the millscale before exposure. Such material has been widely used in North America for highway bridges and for architectural purposes, and also to some extent in the UK and Europe.

After suitable surface preparation, e.g. blast cleaning, low-alloy steels can be coated by paints, sprayed metal coatings, etc. and there is some evidence that such coatings last longer than on mild steel under similar conditions of exposure⁶.

Stainless Steels

There are many grades of stainless steel, and some are virtually non-corrodible under ordinary atmospheric conditions. Their resistance results from the protective and normally self-repairing oxide film formed on the surface. However, under reducing conditions, or under conditions that prevent the access of oxygen, this film is not repaired, with consequent corrosion.

Since stainless steels are generally unprotected, the design points discussed earlier are particularly applicable to them, and features such as crevices should be avoided.

It is recommended that advice be sought when choosing the type of stainless steel to be used. Under severe conditions it may be necessary to use an Fe–18Cr–10Ni–3Mo type, but under milder conditions a much lower grade such as an Fe–13Cr steel may be satisfactory. Frequently the deciding factor will be cost, since in general, the greater the content of alloying metals, particularly Ni and Mo, the higher the cost. The following points should be considered:

1. The environment to which the steel will be exposed.
2. Types and concentration of solutions that may be in contact with the steel. This is particularly important where the failure may be due to local concentrations of dilute solutions. For example, the small chloride content of tap waters is unlikely to cause any trouble, but if it concentrates at the water level due to heating and evaporation of the water, then attack may occur.
3. Operating temperatures and pressures.
4. Mechanical properties required.
5. Work to be performed on the steel.
6. Fabrication and welding techniques to be used. In connection with welding it should be emphasised that the correct grade of steel and electrode or filler rod must be used.

Stainless steel is not generally made in the large sizes offered in the cheaper steels, but a range of sections, tubes, flats, rods and sheet is obtainable. Some savings in thickness and weight are possible, however, because of its superior corrosion resistance. If the strength requirements go beyond the point where the use of stainless steel becomes economic, it is possible to use clad material. Stainless steel is often used as cladding and for window frames, doors, etc. for prestige buildings.

Coated Steel Sheet

Probably the most familiar coated steel sheets are the ubiquitous galvanised corrugated roofing and cladding sheets which have been used for many years, particularly for farm buildings, either painted or unpainted. In addition to zinc other metallic coatings are available, e.g. hot dip aluminium and hot dip aluminium-zinc alloys.

Nowadays, however, zinc-coated steel sheets, either continuously galvanised or electroplated, are often used as a basis material for overcoating with plastic materials or paints. The coatings are usually applied continuously and have a range of uses both externally and internally. Many surface finishes are obtainable, e.g. plain or embossed, and in an extensive range of colours, to suit almost any requirement⁷.

Some of the uses of such precoated materials are roofing, cladding, decking, partitions, domestic and industrial appliances, and furniture. The formability of these materials is excellent and joining presents no problems. The thickness of the coating varies according to the material used and the service conditions which the end product has to withstand.

Vast amounts of continuously galvanised steel sheets are produced, and unless they are painted or otherwise coated, their life depends on the thickness of the galvanising and the service environment in which they are used. Similarly in the case of steel sheets coated with aluminium or aluminium-zinc alloys, their performance is dictated by their coating thickness (see Section 13.4). A problem often associated with such material is corrosion at the cut edges. From work carried out by BISRA and others⁸ it has been shown that providing the bare steel edge is less than 3 mm in width, the amount of corrosion is minimal and the life of the sheet is not adversely

affected, although rust staining will occur. Aluminium and aluminium-zinc alloy coatings are not as effective as zinc coatings in sacrificially protecting cut edges. If staining is important because of the appearance, the cut edge should be orientated so that the stain does not run over the sheet. The edge could, alternatively, be beaded over or painted with a suitable painting scheme. If appearance is important it may be advantageous to paint overall.

Protective Coatings

Zinc, aluminium, aluminium-zinc alloys and other materials such as paints and plastic coatings are often used as protective coatings for steel. These metals act not only as a barrier, but where breaks occur in the coating, corrode preferentially under most conditions and thus sacrificially protect the underlying steel. Aluminium is normally less negative than zinc, but provides adequate sacrificial protection in industrial and marine environments. The corrosion protection afforded by aluminium-zinc alloy coatings lies between that of aluminium and zinc. Two alloys are currently used: 5% aluminium whose properties are more akin to zinc and 55% aluminium which is closer to aluminium. With metal coatings the life expectancy depends on the coating weight, which is generally synonymous with thickness. The thickest coatings are produced by dipping or by spraying, thinner coatings by diffusion and in the case of zinc by electrodeposition (see Chapter 12).

The metal spraying operation using zinc or aluminium as a protective coating is usually followed by a painting scheme. The choice of sprayed metal and paint scheme depends on the service conditions⁹, but normally this type of system is used on prestige buildings or structures, where longevity is of prime importance and maintenance requirements need to be kept to a minimum.

Paint is the most widely used protective coating for steelwork and normally acts as a barrier between the metal and environment. The choice of type of paint and the final thickness required depends on the conditions of service, and the more severe the conditions the thicker and more resistant the paint film needs to be. Also the more sophisticated the paint system the more demanding is the surface preparation required.

Often steelwork will initially be painted before final fabrication, and problems that may arise when maintenance painting becomes necessary may not

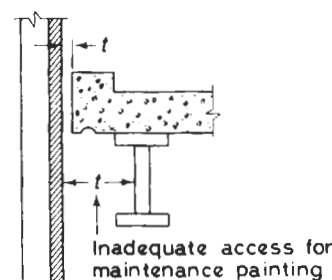


Fig. 9.18 Access for maintenance

be fully appreciated¹⁰ (see Fig. 9.18). The 'I'-beam can be painted in the shop, but access for maintenance may be inadequate and either the distance t should be increased or the gap closed so that maintenance is not required. An actual case of failure occurred where the rolled steel joists carrying the floor of a refrigeration chamber were placed so close together that they could not be reached for painting¹¹. Heavy condensation led to dangerous rusting on the inner surfaces of the joints and in consequence the steelwork had to be replaced prematurely (Fig. 9.19).

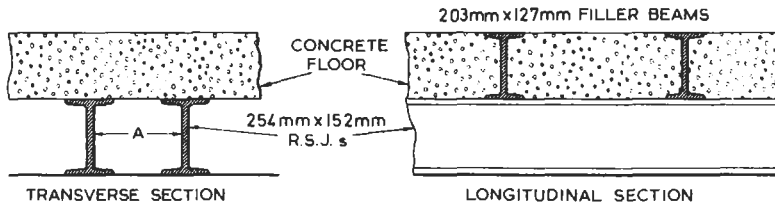


Fig. 9.19 Design of reinforced concrete floor. For the old joists A was 7 in (178 mm) leaving a 1 in (25 mm) gap between the toes; for the new joists A was increased to 18 in (457 mm)

Designers should always bear in mind the necessity to inspect and maintain all parts of a structure that may be corroded and should provide adequate access for these purposes.

The choice of protective system will be determined by many factors such as the importance of the structure, the environment and its proposed life. Having chosen a suitable system or systems¹², it is essential that requirements including adequate inspection are specified exactly, and that there is the fullest possible collaboration between the paint suppliers, the contractors, the architects and all other parties concerned. It is not always appreciated that the life of a coating depends not only on the material but also on other factors such as surface preparation and the application of coating to give the required dry film thickness. A duplex coating of a cathodic coating and an organic coating may well have a life greater than the sum of the expected life of both coatings.

Bimetallic Corrosion

When other metals are used in conjunction with steel, careful consideration must be given to the possibilities of galvanic attack (Section 1.7).

The rate of corrosion and damage caused to the more negative metal will depend upon the relative sizes of the anodic (corroding metal) and cathodic areas. A small anode and a large cathode will result in intensive corrosion of the anodic area. On the other hand, if the anode is large compared with the cathode, the corrosion of the anodic area will be more general and less likely to result in rapid failure. For example, a steel rivet in a copper plate will be rapidly attacked in sea-water, whereas a copper rivet in a steel plate may lead only to slightly accelerated corrosion of the steel in the area adjacent to the rivet. Prediction of the rate of corrosion of the less noble metal

in a galvanic cell is difficult, but there is always the possibility of serious trouble if two dissimilar metals are in contact, particularly under immersed conditions. The safest way of avoiding this is to ensure that dissimilar metals are not in contact. If this is impracticable, the following will help to reduce or stop attack on steel:

1. Use more noble metals for fastenings.
2. Insulate the metals from each other by suitable gaskets, washers, etc.
3. Paint the surfaces of both metals. Avoid painting only the less noble metal because if the coating is damaged severe attack may result at the damaged area.
4. Prevent moisture dripping from the more noble metal on to the less noble metal.

From the reversible potential of zinc, accelerated corrosion would be expected to occur when zinc is coupled with many other metals commonly used in buildings. Aluminium, contrary to its reversible potential, is generally found to be slightly cathodic to zinc and is protected when the two metals are coupled together, as when aluminium sheet is fixed with galvanised nails. In practice, although some small acceleration in the corrosion rate of zinc will be expected in the immediate area of contact with another metal, the effect is usually severe only when it is in contact with copper. For example, where zinc and aluminium gutters or zinc and cast-iron gutters are fitted together, very little accelerated corrosion of the zinc is normally found. Brass¹³, with its 30–40% zinc, is very much less active than copper, and brass screws and washers can be used for fixing zinc with little or no accelerated corrosion troubles; but with copper, rapid failure occurs.

Drainage water from copper affects zinc in a similar way. Zinc sheets must never be fixed with copper nails, nor should copper roofs drain into zinc or galvanised gutters. Copper lightning arrestors provide further potential hazards to zinc work; when a copper lightning strip has to pass over or near a zinc roof, it should be either well insulated or heavily tinned.

Non-ferrous Metals and Plastics

For some purposes where the strength and ductility of steel are not pre-requisites, other metals or materials may be used to advantage, particularly when the component or article is not a load-bearing one. Some of the non-ferrous metals and plastics materials are extremely useful in this respect, especially the latter with their excellent corrosion-resistant properties and ease of formability. Non-ferrous metals in sheet form are often used as roof covering. In such situations they could well become subject to condensation. Condensation could be the result of thermal pumping or internal conditions. Under conditions in which condensation can occur, copper is not normally attacked, but lead, zinc and aluminium may be attacked and corrode from the inside of the building outwards.

Copper¹⁴ Although copper is weather-resistant under normal conditions of exposure, certain precautions are necessary to avoid the risk of premature failure. For instance, copper that is exposed to high concentrations of flue

gases, as may happen within a metre or so of chimney exits, may become corroded within a relatively short time. To avoid this the chimney should be built to a reasonable height above the roof. For similar reasons ventilators should not be made of copper where highly sulphurous fumes may be encountered. The use of potentially corrosive materials as underlays for copper roofing may also result in failure.

Bare copper exposed indoors will slowly tarnish. Transparent lacquers may be used, however, to retain a bright surface without the need for frequent cleaning. Neither copper nor any copper alloy will remain bright and polished without maintenance or coating.

Lead¹ Corrosion of lead gutters and weatherings is usually associated with slate roofs on which vegetable growth such as algae, moss or lichen is present. These produce organic acids and carbon dioxide which significantly increase the acidity of rain water running over the roof. New cedar-wood shingles also contain acids which are slowly washed out by rain, thus intensifying the attack that would in any case slowly occur owing to vegetable growth on the roof. Probably the simplest way of avoiding this type of failure is to protect the lead with a thick coating of bituminous preparation extending well underneath the edge of the roof.

Lead is relatively easily corroded where acetic acid fumes are present and under such conditions it either should not be used or should be efficiently protected. Generally, any contact between lead and organic material containing or developing acids will cause corrosion; for instance, unseasoned wood may be detrimental. Trouble from this cause may be prevented by using well-seasoned timber, by maintaining dry conditions, or by separating the lead from the timber by bitumen felt or paint. Lead is also subject to attack by lime and particularly by Portland cement, mortar and concrete, but can be protected by a heavy coat of bitumen. A lead damp-proof course laid without protection in the mortar joint of a brick wall may become severely corroded, especially where the brickwork is in an exposed condition and is excessively damp.

Aluminium The resistance of aluminium and certain of its alloys to atmospheric corrosion is fairly high. Nevertheless, corrosion does occur, especially on under-surfaces, e.g. of bus shelters. Normally, in simple exposure the corrosion reaction stifles itself and the rate falls to a low value. With a few alloys, however, atmospheric corrosion may lead to severe attack, and layer corrosion may occur. It is important therefore to pay attention to materials, design and protection. Intermetallic contacts, crevice conditions, horizontal surfaces, etc. should be avoided. Materials for sections, plate and sheet, where strength is important, should be restricted to primary alloys. All heat-treated alloys should be painted, using first a chromate priming paint containing not less than 20% zinc chromate pigment, or an equivalent chromate paint. Crevices should be packed with a suitable composition such as chromate jointing compound or impregnated tape. By paying attention to these points, aluminium should behave satisfactorily.

Zinc Zinc surfaces corrode more slowly in the country than in either marine atmospheres or in industrial areas where sulphur pollution constitutes the main danger both to them and to many other building materials.

Sulphur and its compounds in the air can become oxidised to sulphuric acid; this forms soluble zinc sulphate, which is washed away by rain¹³.

The purity of the zinc is unimportant, within wide limits, in determining its life, which is roughly proportional to thickness under any given set of exposure conditions. In the more heavily polluted industrial areas the best results are obtained if zinc is protected by painting, and nowadays there are many suitable primers and painting schemes which can be used to give an extremely useful and long service life under atmospheric corrosion conditions. Primers in common use are calcium plumbate, metallic lead, zinc phosphate and etch primers based on polyvinyl butyral. The latter have proved particularly useful in marine environments, especially under zinc chromate primers¹⁵.

Zinc has been used extensively as a roofing material, but its life, especially in industrial areas, is somewhat dependent on the pitch or slope of the roof; those of steep pitch drain and dry more rapidly and therefore last longer. Irrespective of the locality, exterior zinc-work may fail prematurely if the design is unsuitable or the installation faulty. Many failures arise from a combination of purely mechanical reasons and secondary corrosion effects, white-rusting being the most important of these. This tendency can, however, be reduced by chromating. When used inside factories¹⁶ zinc coatings have been found to be satisfactory in withstanding attack by many industrial gases and fumes. The protection of fabricated structural steelwork by hot-dip galvanising as is used in current constructions, has allowed lightweight concrete-clad steel sections to be used with complete safety.

Zinc in contact with wood Zinc is not generally affected by contact with seasoned wood, but oak and, more particularly, western red cedar can prove corrosive, and waters from these timbers should not drain onto zinc surfaces. Exudations from knots in unseasoned soft woods can also affect zinc while the timber is drying out. Care should be exercised when using zinc or galvanised steel in contact with preservative or fire-retardant-treated timber¹⁸. Solvent-based preservatives are normally not corrosive to zinc but water-based preservatives, such as salt formulated copper-chrome-arsenic (CCA), can accelerate the rate of corrosion of zinc under moist conditions. Such preservatives are formulated from copper sulphate and sodium dichromate and when the copper chromium and arsenic are absorbed into the timber sodium sulphate remains free and under moist conditions provides an electrolyte for corrosion of the zinc. Flame retardants are frequently based on halogens which are hygroscopic and can be aggressive to zinc (see also Section 18.10).

Zinc-alloy diecastings used indoors Zinc-alloy diecast fittings have good corrosion resistance. Generally, such castings may be used in buildings without further protection by painting, but it is of advantage, especially where conditions of permanent dampness may occur, that they should be chromate-treated or phosphated, and then enamelled, or coated with an etch primer and painted after installation. Where a chromium-plated finish is used, it is important that an adequate basis of electroplated copper and nickel plating is provided.

Soluble sulphates and chlorides in brickwork, plaster and other walling materials provide a more serious source of corrosion under damp condi-

tions. Under such circumstances, or where zinc or zinc-alloy fittings are to be placed in contact with breeze, concrete or black ash mortar (made from ground ashes) the metal may be protected with two coats of hard-drying bitumen paint.

Zinc as a protective coating to building components Perhaps the most important use of zinc in building is as a protective coating to steel. In spite of the initial cost, a substantial coating of zinc (or of aluminium) is of great value, and often saves the cost of remedying troubles caused by corrosion. For general purposes it can be accepted that the effectiveness of the coating depends on the weight of zinc coat applied and not on the method of application.

Metals in Contact with Concrete

Little information is available about the corrosion of metals in concrete, although it seems likely that all Portland cements, slag cement and high-alumina cement behave similarly¹⁷. Concrete provides an alkaline environment and, under damp conditions, the metals behave generally as would be expected; e.g. zinc, aluminium and lead will react, copper is unaffected, while iron is passivated by concrete.

Aluminium reacts vigorously with a wet, freshly prepared concrete mix and the reaction, in which hydrogen is evolved, has been used for preparing lightweight cellular concrete. When the concrete has set, however, its reactivity is reduced. The degree of corrosion experienced by aluminium depends upon its alloy type¹⁹. Whilst the extent of corrosion may not reduce the structural strength of the aluminium, the more voluminous corrosion product formed can lead to cracking and spalling of the concrete.

Zinc will initially react with cement-based materials with the evolution of hydrogen. This reaction can be controlled by the presence of soluble chromate either in the cement (over 70 ppm) or as a chromate passivation treatment to the zinc surface. Zinc can therefore be used to provide additional protection to steel in concrete. It is more effective in carbonated concrete than in chloride-contaminated concrete.

The reaction of lead with concrete differs from that of aluminium and of zinc in that it is not normally rapid during the early wet stage. It is, however, progressive in damp conditions, and this is said to be due to the fact that the concrete prevents the formation of a protective basic lead carbonate film on the surface of the lead. The packing of lead cables in plaster of Paris is reported to be of doubtful value in preventing corrosion from surrounding concrete.

Little information is available on the performance of copper and of copper alloys in contact with concrete, but concrete sometimes contains ammonia, even traces of which will induce stress-corrosion cracking of copper pipe. The ammonia may be derived from nitrogenous foaming agents used for producing lightweight insulating concrete.

The corrosion behaviour of iron and steel in contact with concrete is of great importance, not only because of the amount of metal involved, but also because the metal is frequently load-bearing, and the stability and

durability of a structure may depend upon the control of corrosion. The alkaline reaction of the adjacent concrete may, however, damage sensitive paints and protective finishes. The corrosion of steel reinforcements in concrete is discussed below.

Effects of Composition of Concrete

Concrete²⁰ made with ordinary Portland cement is an alkaline material having a pH in the range 12.6–13.5. Steel embedded in such a material will be passive. However, like most alkaline materials concrete will react with the acid gases in the atmosphere, e.g. sulphur dioxide, carbon dioxide with a reduction in alkalinity. Carbon dioxide is the reactant which effects a chemical change in the concrete reducing the pH to a level at which steel is no longer passive. This process is known as carbonation. Carbonation spreads in from the surface of the concrete and when the carbonation front reaches the steel the steel is at risk from corrosion. The rate at which carbonation occurs depends upon the porosity, permeability, cement content, water/cement ratio and other factors but the depth is normally proportional to \sqrt{t} . The depth of concrete cover to the steel reinforcement therefore has a significant bearing on the corrosion protection provided by the concrete to the embedded steel. In general terms the thicker the cover the longer the concrete provides protection to the steel.

Unfortunately, the protection provided by concrete can be overcome by contamination of the concrete by chloride. Chloride, when entering the concrete as a contaminant of the mix constituents, is to a large extent (about 90%) complexed within the cement matrix and only a small percentage is free in the pore solutions. The present codes of practice²¹ ban the use of chloride-bearing additives and restrict the amount of chloride present in concrete. For normally reinforced concrete made with ordinary Portland cement it should be not more than 0.4% chloride ion with respect to the cement content weight/weight.

When mature concrete is contaminated by chloride, e.g. by contact with deicing salts, the cement chemistry is more complex, and less chloride is taken up by the cement hydrate minerals and a larger proportion is free in the pore solutions and can therefore pose a greater hazard. When embedded steel corrodes, the production of a more voluminous corrosion product pushes the concrete from the steel with resultant cracking and spalling of the concrete.

There is no objection to the use of slag aggregates for reinforced concrete provided the slag meets the various sulphur-content specifications, and similar considerations apply to lightweight aggregates, although it has been claimed¹⁹ that the sulphur content of blast-furnace slag is not dangerous. Clinker aggregates, on the other hand, are not permitted in the UK because they cause corrosion of reinforcement. The corrosiveness of clinker and boiler slag is due probably to the high sulphur content.

The Corrosion of Steel Reinforcements in Concrete

Normal Reinforcement

In the middle of the last century, the tensile properties of concrete were improved by the introduction of steel to reinforce the concrete. This practice has developed since then to such an extent that reinforced concrete is now one of the major structural materials used in construction. In general it has proved to be a good durable material with some of the structures erected at the turn of the century still providing satisfactory service in the late 1970s.

Normally concrete is reinforced with plain carbon steel, but under conditions where rapid carbonation can occur or there is a risk of chloride contamination, corrosion-protected or more corrosion-resistant reinforcing steels may be necessary. Currently there are three reinforcing bars which have enhanced corrosion resistance:

1. Galvanised steel²² provides increased corrosion resistance in carbonated concrete. In concrete with more than 0.4% chloride ion with respect to the cement content, there is an increased risk of corrosion and at high chloride contents the rate of corrosion approaches that of plain carbon steel. In test conditions the rate of corrosion is greater in the presence of sodium chloride than calcium chloride.
2. Fusion-bonded epoxy-coated steel²³ performs well in chloride-contaminated concrete up to about 3.9% chloride ion in content.
3. Austenitic stainless steels²⁴ resist corrosion at levels of chloride contamination greater than that which can be resisted by epoxy-coated bar.

Prestressed Reinforcement

For prestressed concrete, either high-tensile steel wires or occasionally bars of steel alloy containing manganese and silicon, can be used. Galvanised wires may also be used for prestressed concrete, but it is recommended that they be chromated before use.

In a normal reinforced concrete structure, the tensile stress in the steel is comparatively low, but in prestressed concrete the steel is held permanently in tension with a stress equivalent to about 65% of its breaking load. It is necessary, therefore, in prestressed concrete, to consider the possibility of the occurrence of stress corrosion. Surface rusting or corrosion of prestressed wires can affect the working cross-sectional area of the reinforcement, and pitting, which might be unimportant on a 12 mm bar, could cause failure on a 2.5 mm diameter stressed wire. The number of reported failures of prestressed concrete due to fracture of reinforcement is very low and in general the behaviour of steel in prestressed concrete is no different from that of steel in ordinary reinforced concrete. Prestressed concrete is made from materials of slender section using higher working stresses than are customary for ordinary reinforced concrete. The concrete is also of a higher quality.

Work carried out at the Building Research Station²¹ suggests that the most significant influences on the corrosion of prestressed steel wire in concrete are: (1) the presence of chloride, (2) the composition of the concrete, (3) the degree of carbonation of the concrete, (4) the compaction of the concrete around the wire ensuring that voids are absent, and (5) chloride promoting pitting attack, leading to plastic fracture and not stress-corrosion cracking of prestressing steel. Gilchrist^{25(a)} considers that prestressing steels may fail by either hydrogen cracking or active path corrosion, depending on conditions; most service failures have been due to hydrogen cracking.

Prestressed steel in concrete should thus be durable if a dense, impervious and uniform concrete free of chloride surrounds the steel and adequate depth of concrete is given to the steel.

Materials in Water-supply Systems

The most important non-ferrous metals for handling water are lead, copper and zinc; the last, however, is used chiefly as a protective coating on steel or alloyed with copper to form brass.

The choice of materials for most applications in domestic water supply is governed by consideration of mechanical properties and resistance to corrosion, but the cost, appearance and ease of installation should also be considered when the final choice has to be made between otherwise equally suitable materials²⁶.

Many plastic materials are also now being used in domestic water systems, in the form of pipes and fittings.

Features that should be avoided for all materials (particularly ferrous metals) in liquid environments and points that should be followed are²⁷:

1. Crevices, because they collect deposits and may promote corrosion by causing oxygen depletion in the crevice, thereby setting up a corrosion cell in which the areas receiving less oxygen corrode at a higher rate.
2. Sharp changes in direction, especially where liquids are moving at high velocities, and re-entrant angles, dead spaces and other details where stagnant conditions may result should be avoided. This is particularly important if inhibitors are to be used.
3. Baffles and stiffeners inside tanks should be arranged to allow free drainage to the bottom of the vessel. The bottom should slope downwards and have rounded corners. Any drain valves or plugs should fit flush with the bottom (Fig. 9.16).
4. Wherever possible different metals should not be connected in the same system. If they have to be used they should be insulated from each other, and the cathodic metals placed downstream of anodic ones.

Galvanised steel pipes Threaded mild-steel tube is the cheapest material for water pipes, but it is not normally used owing to the amount of rust introduced into the water as a result of corrosion. Galvanised mild-steel tube overcomes this problem and may be used for nearly all hard waters, but it is not satisfactory for soft waters or those having a high free-carbon-dioxide content. The ability of a water to form a 'scale' is, therefore, of prime importance when considering the suitability of galvanised steel for an installation.

The Langelier index (Section 2.3) gives useful guidance to this, but it is only an approximation. The scale can be deposited either as nodules covering a relatively small area of metal, or as a thin scale covering a large area. Provided the deposit is not porous, the latter has the greater effect in reducing corrosion, and it has been found that waters derived from rivers tend to form more useful scales than those from wells.

Galvanised steel tubing is cheaper than lead or copper tubing, but is, however, more costly to install because it cannot be bent without damage to the galvanising. A full range of preformed bends, tees, etc. is available, but cutting the tubes to length, threading the ends and screwing up the joints are slow processes. Consequently, a galvanised steel installation is cheap for long straight runs of pipes, but for complicated systems it is liable to be more expensive than copper because of the high cost of installation.

Lead pipes The corrosion resistance of lead is generally excellent, but it is attacked by certain waters. This is usually of little significance so far as deterioration of the pipe is concerned, but is important because of danger to health, since lead is a cumulative poison; even very small doses taken over long periods can produce lead poisoning²⁸. It is for this reason that its use for carrying potable water has been discontinued.

Copper pipes For plumbing above ground, copper is supplied in both half-hard and hard conditions. It has sufficient strength to require only few supports, and can be bent cold, in the small sizes, either by hand or with a portable bending machine. Copper is also supplied in the fully soft condition in coils for laying underground, for heating-panels, etc.

Light-gauge copper tube may be joined by autogenous welding or by bronze welding. These processes, which produce neat strong joints, are usually applied to the larger sizes of tube. For the tubes used for domestic water supply, capillary-soldered fittings, or compression fittings are normally employed.

Two types of corrosion may be experienced. The first is analogous to plumbo-solvency, with the copper being dissolved evenly from the surface of the tube. With some waters²⁹ it is potentially dangerous to use galvanised hot-water tanks and copper pipes. In domestic systems, premature failure of galvanised hot-water tanks connected to copper circulating pipes, due to pitting corrosion of galvanised steel, is encouraged by more than about 0.1 p.p.m. of copper in the water. Failures of galvanised cold tanks due to copper in the water are often the result of back circulation of hot, copper-bearing water in badly designed systems where the cold-water tank is installed too close to the hot-water cylinder. Hot water carried into the cold tank via the expansion pipes when the water is allowed to boil may also sometimes be responsible.

Secondly, under certain conditions copper may suffer intense localised pitting corrosion, leading sometimes to perforation of the tube, in quite a short time. This form of attack is not common and depends on a combination of unusual circumstances, one of which is the possession by the tube of a fairly, but not entirely, continuous film or scale that is cathodic to the copper pipe in the supply water; this can set up corrosion at the small anodes of bare copper exposed at faults or cracks in the film. Carbon films give rise to such corrosion, but since 1950, when the importance of carbon films was

first discovered, manufacturers have taken precautions to avoid as far as possible producing tubes containing them. (See also Sections 1.6 and 4.2.)

Aluminium pipes Aluminium might become an important material for carrying water if its liability to pitting corrosion could be overcome. Very soft waters are difficult to accommodate when normal pipe materials are used, and it is for these that aluminium offers most promise³⁰. The possibility of using it for domestic water pipes, however, appears at present to depend upon finding a cheap and effective inhibitor that could be added to the water, or upon the use of internally clad tube, e.g. Al-1.25 Mn alloy clad with a more anodic alloy, such as Al-1Zn. Such pipes are at present mainly used for irrigation purposes³¹.

Stainless steels Thin-walled stainless steel (Fe-18Cr-8Ni) tubes are now frequently used for domestic installations in place of copper pipe²⁷. Care is required, however, in the design of stainless steel equipment for use in waters with a high chloride content, or where the concentration can increase, since pitting attack may occur. It may also be susceptible to failure by stress-corrosion cracking under certain conditions.

Plastic pipes Pipes made from plastic materials such as unplasticised p.v.c., Polythene, ABS and GRP are now widely used for carrying domestic cold water, wastes and rain water. Joining varies according to pipe diameter and service condition, but is generally relatively simple (see Section 18.6).

Buried pipes Pipes to be laid underground must resist corrosion not only internally but also externally. Light sandy soils, alluvium, or chalk are generally without appreciable action but made-up ground containing a high proportion of cinders is liable to be exceptionally corrosive as also is heavy clay containing sulphates. The latter provides an environment favourable to the growth of sulphate-reducing bacteria, which operate under anaerobic conditions, reducing sulphates in the soil to hydrogen sulphide, and causing severe corrosion especially of steel. Aluminium is believed not to be susceptible to this form of attack, but, like copper or galvanised steel, it is severely attacked by cinders. Wet salt marsh, although it has little effect on copper and only slightly more on lead, causes severe corrosion of galvanised steel or aluminium. These materials are also severely corroded in London clay, in which copper could probably be used unprotected.

When ferrous metal service pipes or piles, etc. are buried in the ground it is advantageous in almost all cases to coat it in some way even if the coating is just a simple dip into a bituminous solution. If, however, the soil is aggressive, or the component is vital or irreplaceable, a more resistant coating should be used, and consideration should be given to the application of cathodic protection (Section 10.4). The coating used can be an epoxide type or something similar, or a plastic coating which is wrapped or extruded onto the pipe wall.

Galvanised steelwork buried in the soil in the form of service pipes or structural steelwork withstands attack better than bare steel, except when the soil is more alkaline than pH 9.4 or more acid than pH 2.6. Poorly aerated soils are corrosive to zinc, although they do not necessarily cause pitting. However, soils with fair to good aeration containing high concentrations of chlorides and sulphates may do so. Bare iron may be attacked five

times more rapidly than zinc in well-aerated soils low in soluble salts, or in poorly aerated soils; and if the soil is alkaline and contains a high proportion of soluble salts the rate may be even higher. Only in soils high in sulphide content does iron corrode less rapidly than zinc.

Plaster and concrete Domestic water pipes are often used in contact with plaster, concrete or flooring materials³². Copper is unaffected by cement, mortars and concrete, which are alkaline in reaction, but it should be protected against contact with magnesium oxychloride flooring or quick-setting materials such as Keenes cement, which are acid in character. Materials containing ammonia may cause cracking at bends or other stressed parts of brass or copper tubes—some latex cements used for fixing rubber flooring come in this category and contact with these should be avoided. Lead is not affected by lime mortar but must be protected from fresh cement mortar and concrete, either by wrapping or by packing round with old mortar or other inert materials. Galvanised coatings are not usually attacked by lime or cement mortars once they have set, but aluminium is liable to be attacked by damp concrete or plaster, even after setting.

Materials for Tanks

Copper hot-water tanks These are usually made cylindrical with domed tops and bottoms, because this form of construction produces a strong tank from light-gauge sheet. They are normally trouble-free except for occasional cases of leakage at the seams, which are usually weltd or overlapped and then brazed. Brazing brasses, containing 40–50% zinc, often give good service, but are susceptible to dezincification in some waters. Dezincification, which is most likely to occur in acid waters or waters of high chloride content, can be avoided if cylinders are brazed with an alloy such as Cu–14Ag–5P. It is more expensive but is fairly ductile, and if used in conjunction with capillary-gap seams, makes an economical as well as a sound job.

In water where copper tanks might be subject to pitting corrosion it is good practice to fit an aluminium rod²⁷ inside the tank. This corrodes sacrificially within the first few months of service, and during this period a protective film is built up on the copper surface.

Galvanised steel hot-water tanks These may be of cylindrical or rectangular form, the latter being popular where space is limited.

In hard or moderately hard waters, galvanised steel hot-water tanks, with galvanised circulating pipes and cast-iron boilers, usually give trouble-free service, but failure by pitting occurs occasionally. Sometimes this is due to extraneous causes, such as rubbish left inside the tank when it is installed. Iron filings left in the bottom of the tank or deposits of inert material are liable to interfere with the formation of the protective scale by the water, and can lead to failure.

Another cause of trouble is overheating, especially during the early life of the tank. Above 70°C a reversal of polarity may take place, the zinc becoming cathodic to the iron. Above this temperature protection of exposed iron is not to be expected. Persistent overheating is frequently the result of fitting

a hot-water tank too small for the heating capacity of the boiler. A lowering of temperature by as little as 5–10°C can add years to the life of a tank. It has also been shown³³ that large-capacity immersion heaters operated intermittently are more beneficial to tank life than small-capacity heaters operated continuously.

Magnesium anodes³¹ suspended inside a galvanised hot-water tank and in electrical connection with it afford cathodic protection to the zinc, the alloy layer and the steel, at high temperatures as well as in the cold. The magnesium is eventually consumed but it is probable that in the interim a good protective scale will have formed on the inside of the tank, so that the magnesium anode will then no longer be necessary. One of the difficulties of this method, however, is the maintenance of a sufficiently even current distribution over the inside of a tank to protect the whole surface, especially in waters of low conductivity. The method is therefore unlikely to be applicable to soft waters.

Cold-water tanks Domestic cold-water tanks are usually made of galvanised steel. As with hot tanks, it is important to avoid leaving filings, etc. in the tank when it is installed and it should be covered to prevent rubbish falling in later. In most waters, galvanised cold-water tanks give good service, the zinc coating protecting the iron while a protective scale is formed. With very soft waters, however, or with waters of high free carbon dioxide content, which do not produce a scale, there may be trouble. Steel or galvanised steel tanks for use in such waters can be protected by coating with bituminous paint or, alternatively, reinforced plastics may be used. For larger cold-water storage tanks, sectional steel or cast-iron tanks protected by several coats of cold- or hot-applied bitumen or bituminous paints are often used. It is important, however, to ensure that all millscale, dirt, etc. is removed before applying the protective coating. Stainless steels can also be used for this purpose.

Cold-water tanks made from Polythene or GRP are generally available, especially in domestic sizes, and are now often used in domestic installations.

Water Fittings

Brass water fittings give no trouble except that dezincification may occur in acid waters or waters of high chloride content, especially when hot. This dezincification has three effects. Firstly, the replacement of brass by porous copper may extend right through the wall of the fitting and permit water to seep through. Secondly, the zinc which is dissolved out of the brass may form very voluminous hard corrosion products and eventually block the waterway—this is often the case in hot soft waters. Thirdly, and often the most important, the mechanical properties of the brass may deteriorate. For instance, a dezincified screwed union will break off when an attempt is made to unscrew it and a dezincified tap or ball-valve seat is readily eroded by the water.

Brass water fittings are normally produced from two-phase brass by hot pressing. Unfortunately this material is vulnerable to dezincification in certain water areas. In areas where the hot pressed fittings are vulnerable,

fittings manufactured from single-phase brasses containing 0.3% arsenic or other non-dezincifiable alloys should be used.

Plastic water fittings ranging from taps to lavatory cisterns are now available and are gradually replacing items previously made in metal in the domestic field, especially in situations where condensation is the cause of unsightly corrosion products.

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9.4 Design in Marine and Offshore Engineering

The field of marine and offshore engineering has massively expanded in recent times, due principally to the remarkable growth of the offshore oil and gas industry. Since the world's first steel offshore oil and gas installation was commissioned in the Gulf of Mexico in 1947, the continental shelf areas of the oceans now provide approximately 25% of the world total oil and gas production. Looking ahead, there will be a continuing development of the continental shelf areas together with exploitation of significant oil and gas reserves in certain deeper ocean basin areas of the world. These factors allied to a general decline in productivity of established onshore production provinces, will result in the proportion of oil and gas produced offshore continuing to rise steadily.

There are, of course, many strong engineering links between the long-established marine engineering industries and the newer offshore engineering industries. Today, there are many hundreds of fixed offshore oil and gas production platforms, drilling rigs and other forms of support installations around the world which require extensive and often costly programmes of maintenance and repair. Carbon-manganese steels dominate marine and offshore structural and process applications largely by virtue of their excellent range of mechanical properties, good availability and cost considerations. However, they are not particularly corrosion resistant in aqueous saline media, and corrosion protection of these steels has to be provided by effective coatings (including cladding and sheathing), cathodic protection or corrosion inhibitor treatments, depending upon circumstances. However, such protection schemes may cost many millions of pounds, both in terms of primary design and installation cost, and in terms of downstream maintenance and other ongoing commitments and costs arising at some later stages of the installation life. The design priority is thus to ensure that a functional and secure design will be suitably productive and be maintained at reasonable cost for the duration of the installation's life.

The vast majority of corrosion design issues faced in marine and offshore engineering involve water in one form or another. In that regard, the two principal media involved are seawater and formation waters (oilfield brines). Seawater, of course, surrounds offshore installations though may also be used as the medium in reservoir injection and other critical offshore process

applications. Hence it is desirable that both structural and internal process corrosion issues be faced at the design stage. There are four main structural corrosion design zones in the marine environment: atmosphere, splash/tidal, immersed and mud. Of these, the splash/tidal zone is by far the most aggressive environment. For example, unprotected low-alloy steels may show mean annual corrosion losses in the atmosphere and immersed regions of around $100 \mu\text{m/y}$, whereas in the splash/tidal regions, it may be as high as $625\text{--}875 \mu\text{m/y}$ depending upon design detail, location, the presence of floating debris or ice, and temperature of the metal's surface. Consequently, corrosion protection measures in this zone on ships, semi-submersibles, drilling rigs and fixed production platforms require to be of the very highest and durable specification. The mud zone may or may not be a zone of serious corrosion hazard, depending upon whether or not anaerobic bacterial action is taking place. Bacterial levels and activity should be checked before installing buried pipework, piling, etc.

Formation water occurs naturally with virtually all oil and gas reservoirs, and is constitutionally similar to seawater in many respects. From a corrosion point of view, however, it differs notably in the following respects:

1. It is generally more saline than seawater. Most North Sea formation waters have salinities two to three times that of seawater.
2. It is anoxic.
3. It has a very low sulphate ion concentration.

Additionally, there may be CO_2 , H_2S or bacteria present, all of which substantially increase the corrosivity of formation waters. Furthermore, whilst in a 'young' oil and gas well the levels of produced formation waters (termed 'watercut') may well be very low, at later stages of maturity, the watercut may reach values in excess of 90%. Consequently, oil and gas production systems may often be subject to increasing corrosion risk with time.

The principal features of seawater and formation waters affecting the marine and offshore corrosion engineering design progress are discussed in the following sections.

Chloride ion concentration Chloride (and indeed bromide and iodide) ions in sea or formation waters are particularly aggressive and troublesome species. They participate in depassivation corrosion processes on alloys such as chromium and chromium–nickel steels, aluminium and titanium alloys, particularly in the absence of oxygen. In addition, many chloride corrosion products which may be formed are highly water soluble, hence little protection is afforded to the metal surface being corroded. Conjoint corrosion phenomena such as stress corrosion cracking and corrosion fatigue may also be exacerbated in the presence of chloride—particularly at elevated temperatures as in oil and gas production situations—though this, of course, depends upon the operating circumstances of the exposed material.

Chlorides are often found as the salt aerosols of the atmosphere, and consequently may strongly influence the corrosion performance of structures and plant, particularly in marine or coastal situations. This influence on corrosivity reduces proportionately with distance from the seawater surface¹, though local environmental factors such as prevailing wind direction, level

of other atmospheric pollutants such as carbon, nitrogen and sulphur dioxides, patterns of precipitation and relative humidity are also influential factors which must be considered when determining the overall corrosivity of a particular location, and hence the materials and/or protection scheme(s), if any, which require to be used².

It is also remarkable how much chloride and other salt aerosol components are ingested into air-consuming systems in offshore installations and aircraft flying over or operating near seawater on a regular basis³. In particular, the massive air-consumption requirements of gas turbine engines used for pumping or power generation applications on offshore installations, and for powering helicopters and fixed-wing aircraft, renders these units highly vulnerable to corrosion problems associated with salt aerosol ingestion, such as fluxing of passive films on nickel-based turbine blades and pitting of aluminium alloy compressor blades. The pervasive nature of salt aerosol components, also appears to have played some part in the world's worst helicopter disaster off Sumburgh in the Shetland Isles in November 1986, when a helicopter servicing offshore oil and gas platforms in the North Sea crashed killing 45 persons on board. A critical gearwheel in the forward transmission of this aircraft displayed what appeared to be fretting corrosion in part due to the primary ingress (and entrapment) of salt⁴ (Fig. 9.20).

Oxygen concentration Oxygen concentration is important in a number of respects. When it is high, it generally ensures that the cathodic reaction for

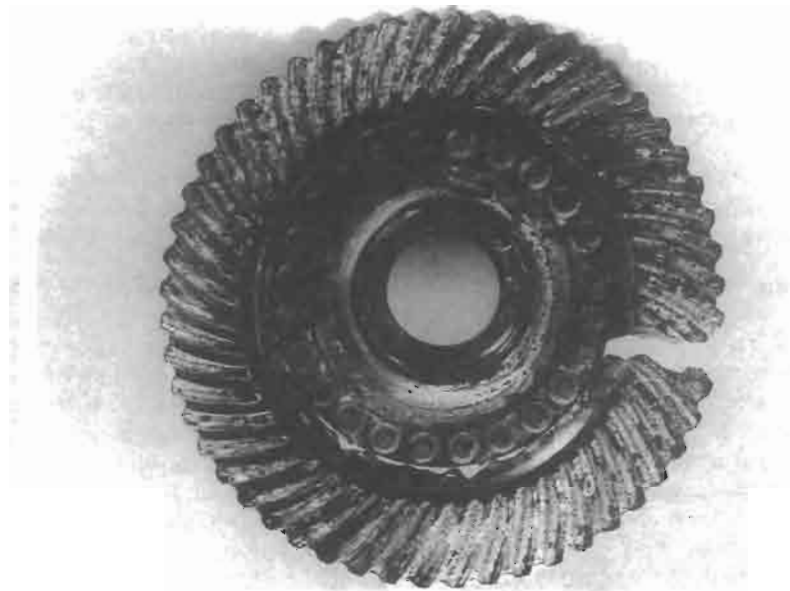


Fig. 9.20 Spiral bevel ring gear assembly from the forward transmission gear box of Boeing Vertol 234-LR (Chinook) aircraft registration G-BWFC which crashed into the sea off the Shetland Isles in 1986. Note the peripheral and radial fractures in the gear, which appeared to be responsible for the crash. There was evidence of fretting and galvanic corrosion which may have been responsible for initiation of the fracture sequence

most situations (and certainly in seawater within the normal pH range of 7.6 to 8.2) is one of oxygen reduction viz:



This reaction proceeds rather sluggishly under most circumstances, and the accompanying production of hydroxide ions (which may have the effect of raising the pH and partially-passivating adjacent surfaces) results in this reaction being the rate-limiting corrosion reaction in seawater. Under certain circumstances, oxygen reduction is replaced or is accompanied by the hydrogen-evolution cathodic reaction which brings much more serious consequences such as accelerated corrosion rates, hydrogen embrittlement, disbonding of coating systems and, of course, fire or explosion hazard. The hydrogen-evolution cathodic reaction is promoted in seawater media which:

1. are anaerobic or anoxic;
2. have a lower pH than normal;
3. host a metal surface held at excessively negative cathodic potential during cathodic protection operations.

However, dissolved oxygen ensures that passive films are maintained on passivating metals and alloys. Conversely, in anoxic waters where there is no alternative supply of oxygen, corrosion rates of passivating metals and alloys may rise dramatically and are often manifested by severe pitting attack¹. However, in the case of non-passivating alloys such as carbon-manganese steels, corrosion rates will be reduced. It is important to stress that in anaerobic or anoxic waters, there will be a greater risk of sulphate-reducing bacteria becoming active, producing hydrogen sulphide, and increasing corrosion rates on affected surfaces⁵. Consequently, the use of biocides or biostats should be carefully considered in such situations.

Electrical resistivity The low electrical resistivity of seawater (and even lower values for formation waters) results in two important corrosion and corrosion-protection consequences:

1. It enables greater cathodic/anodic surface area ratios to become active in corrosion processes, thereby promoting pitting mechanisms in vulnerable materials.
2. It enables cathodic protection to be applied with relative ease.

Scaling properties The feature of precipitating scales in seawaters and formation waters may bring corrosion advantages or disadvantages depending upon circumstances. For example, the scaling of tube walls in heat exchangers or process coolers may reduce heat transfer rates and thermal efficiencies in such systems. Oil- and gas-well tubing may also be subject to scaling as a consequence of injection water breakthrough in a complex reaction with formation waters from the reservoir rock itself. This scaling may be so extensive as to plug the voids in the reservoir rock, and reduce the bore of the well tubing — both of which can seriously reduce well production rates. However, where such tube scales are coherent and intact, they can provide effective corrosion protection to affected surfaces.

Cathodic protection in seawater also results in the precipitation of a calcareous scale on the metal surface (due largely to the increase in pH (see equation 9.1)) and the scale has a largely beneficial effect in three respects.

1. It helps 'spread' the cathodic current over a greater area of surface.
2. It reduces current requirements for maintenance of a particular cathodic potential, thereby reducing costs.
3. It provides some temporary and partial corrosion protection should the cathodic protection system become ineffective for any reason.

Marine fouling Marine fouling is a design issue *only in seawater* and is largely determined by two factors, the first of which is the composition and nature of the exposed surface. Certain alloys such as the cupronickels, have antifouling properties in normal exposure circumstances allowing slow copper dissolution, whereas steels foul rapidly and heavily when corrosion is not proceeding rapidly. In addition, if the design of the surface is such as to produce quiescent havens of low water velocity, or are 'rough' in surface finish, then marine fouling will amass quickly and heavily. The second factor determining fouling is the zone of exposure. Marine fouling only amasses in continuous and possibly very thick films in the surface layers of seawater, hence seawater intakes (or other engineering artefacts which are required to remain substantially free of fouling) should be placed at depths of around 70 m or greater, where, at worst, only discontinuous and thin foulant cover may occur.

Most of the published evidence suggests that marine fouling cover—particularly where it is continuous and well established—reduces corrosion rates of steels⁶⁻⁸. Indeed, 35‰ seawater is by no means the most corrosive of saline environments towards steel. Brackish water, as found in estuarine or certain other coastal areas, is considerably more aggressive towards steel⁶, and careful design measures should be taken to ensure that effective corrosion control is achieved in such circumstances.

Design Principles

The broad principles of design that should be followed in order to effectively and economically control corrosion in marine and offshore engineering should also be subject to the overriding necessity to regard designing against corrosion as an integral part of the total planning and costing procedure which should be continuously followed at all stages from the initial plans to the finished construction. Failure to do so is likely to result in breakdown of plant (with consequential losses), costly maintenance or modifications in design (if these are practicable) and a possible reduction of safety factors. An attempt to design against corrosion as an afterthought is generally unsatisfactory, costly and often impractical.

Whilst careful design and informed forethought can often minimise or even prevent corrosion at little extra cost where the environmental conditions or the conditions of service are severe (as in most forms of marine and offshore engineering) reliable, secure and cost-effective corrosion control cannot be effectively achieved without considerable expense, although even in these circumstances good design can help to significantly reduce this. In

general, the extra initial outlay involved in building structures and equipment with a level of corrosion resistance, protection or control appropriate to the service conditions concerned and the length of life required, more than compensates for the downtime, trouble and cost that stem from employing cheaper materials of inadequate resistance or with inadequate protection. Many corrosion problems may also arise through poor or inadequate QA/QC procedures.

The main principles to be observed can be summarised as follows:

1. Features that apply, entrap or retain corrosive agents such as water, water vapour and aggressive ions should be strenuously avoided. This can be done by (a) attention to the geometry of designs and methods of construction, (b) by the provision of adequate drainage, (c) by protection against contact with hygroscopic, absorbent and/or corrosive materials, and (d) by methods of preventing or reducing such entrapment such as changing operating conditions or dehumidifying (Figs. 9.21 and 9.22).

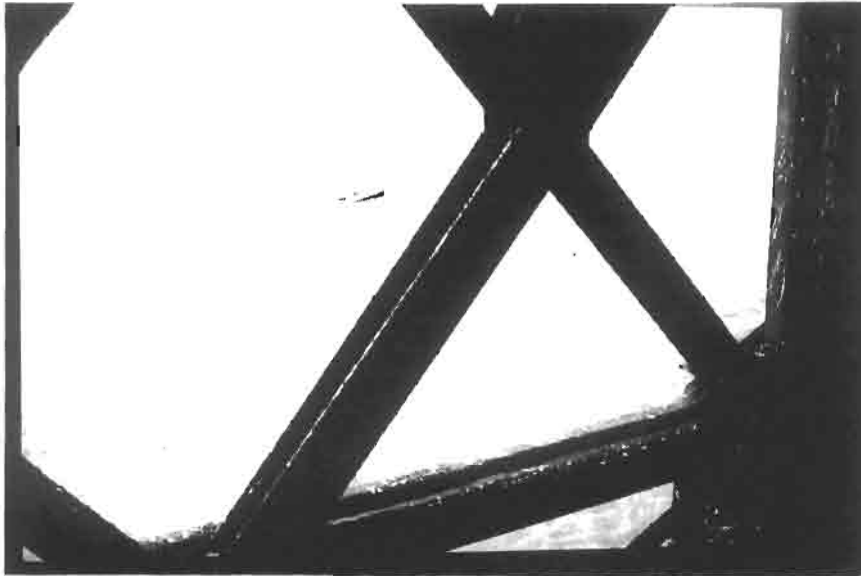


Fig. 9.21 Water trap in steel girder assembly of a bridge. Salt aerosol, bird excrement, etc., may also find their way into this stagnant water, producing an extremely corrosive fluid

2. Where appropriate, designs should facilitate the application of adequate corrosion-protection systems that can be readily maintained. This can be achieved by attention to the geometry of the initial and any retrofitted design and methods of construction, and by making provision for good inspectability and accessibility.
3. All methods of corrosion control such as careful materials selection, including coating and cladding, inhibition and cathodic protection, should be regarded as an integral part of the design process.



Fig. 9.22 Water/steam vent from a chemical plant cooling system. Note that venting water and condensed steam drips onto the lower surface, producing corrosion problems that would not exist if the vent were placed in a location not likely to create such problems

4. Care should be exercised in the use of dissimilar metals in contact or in close proximity. If dissimilar metals must be used, they should be insulated from one another so far as is practicable. Alternatively, if they cannot be insulated, the use of a 'middle piece' with a suitable potential may be effective⁹. In any event, where a galvanic couple exists, the more active metal should have the greater exposed area.
5. Seawater systems should be designed to avoid excessive water velocities, turbulence, aeration, particulates in suspension, rapid changes in piping section and direction. Likewise, extended periods of shutdown should also be avoided since stagnation of contained seawater, will result in bacterial activity and H_2S production with consequential and perhaps serious corrosion and health and safety problems.
6. Undue static or cyclic stressing and other features which give rise to stress concentrations should be avoided as these may lead to premature failure by stress-corrosion cracking or corrosion fatigue.

7. So far as possible, components that operate in highly turbulent-flow conditions should be designed with a view to eliminating cavitation and/or impingement erosion attack.
8. Designs should have regard to the material being employed, e.g. designs and methods of fabrication or construction suitable for steel will not be directly transferable to, or appropriate for, aluminium alloys or glass-reinforced plastics.
9. Welded joints should be ground flush to enable good coating adhesion and performance. In addition, weld metal should be selected such that it is cathodic to the parent material(s) being welded (Fig. 9.23).
10. Use of material with good pitting corrosion resistance is desirable in seawater and oilfield brine (formation water) media.

Some examples of how these principles should be applied, are described in the following pages.



Fig. 9.23 Welded areas of an offshore platform structural tubular displaying premature corrosion due to (a) lack of surface grinding (resulting in poor paint adhesion and performance) and (b) the fact that the weld metal is anodic relative to the parent material of the tubular

Avoidance of Entrapment of Corrosive Agents

Many factors influence the corrosion of metals in the atmosphere, including the natural phenomena that make up the vagaries of climate and weather. Of these, the feature of greatest importance is moisture in its various forms, since, other factors apart, the amount of corrosion that takes place is largely a question of whether and how long a period the surface of the metal is wetted ('time of wetness').

Although the corrosivity may not be high provided the condensed moisture remains uncontaminated, this rarely happens in practice, and in marine environments sea salts are naturally present not only from direct spray but also as wind-borne particles. Moreover, many marine environments are also contaminated by industrial pollution owing to the proximity of factories, port installations, refineries, power stations and densely populated areas, and in the case of ships' or offshore installation superstructures by the discharge from funnels, exhausts or flares. In these circumstances any moisture will also contain S, C and N compounds. In addition, solid pollutants such as soot and dust are likely to be deposited and these can cause increased attack either directly because of their corrosive nature, or by forming a layer on the surface of the metal which can absorb and retain moisture. The hygroscopic nature of the various dissolved salts and solid pollutants can also prolong the time that the surface remains moist.

Designs should therefore avoid, as far as possible, all features that allow water (whether seawater, rainwater or moisture from any source) to be applied, entrapped or retained. These conditions are not only corrosive towards bare metals; they also adversely affect the life of protective coatings both directly and by the fact that it is often difficult at areas subject to these conditions to give sound and adequate surface preparation for good paint adhesion and subsequent performance.

Good designs in these respects do not differ for metal structures exposed in marine environments from those for similar structures exposed elsewhere, several examples of which are illustrated elsewhere in this text and in Reference 9, but the frequent presence of seawater or salt-contaminated water makes observance of these designs especially necessary. The same principles also apply to ships or offshore installation superstructures and internal fittings, although there are many sites where it is impossible to ensure that water cannot collect and be retained. A few of many examples are ventilation shafts or ducting that is subject to the ingress of spray or rain, areas around wash-deck valves, junctions of mushroom ventilators with decks, junctions of horizontal stiffeners with vertical plates, and behind the linings of bathrooms, wash areas and under bulkhead and deck coverings. In these areas either extra protection should be given or designs should allow, so far as is practicable, ready accessibility for frequent inspection and/or maintenance.

Bilges and ballast waters are one of the most difficult areas of this nature to deal with, especially in machinery spaces, since not only are they almost impossible to keep dry or even to dry out while the offshore installation is in operation, but effective maintenance of protective coatings at all areas is in any case quite impossible except at major overhauls and refits, because of inaccessibility or very high temperatures and humidities. Good initial

protection of these areas by a well-applied coating system during building when all surfaces are fully accessible considerably reduces subsequent maintenance problems. Designs can help by arranging for bilge water to collect in sumps or separator vessels where it can be completely drained or pumped away. Alternatively, some authorities favour the use of cathodic protection with sacrificial anodes, but this is only effective if an adequate amount of water is present and if it has a low electrical resistivity. In addition the facility to inspect and retrofit anodes should be available. The method may also become ineffective by the anodes becoming coated with oil or grease, being painted inadvertently, or removed through use or mechanical damage.

Another common cause of a metal surface remaining wet is contact with absorbent materials, particularly insulants such as rock-wool, and this again can cause serious attack when seawater or chloride-contaminated water becomes entrained. In addition, the absorbent material itself can be (or may become) corrosive, as in the case of wood. Examples of trouble that can occur from this cause are wooden decks or fenders laid over steel, certain aluminium alloy frames in contact with wooden hulls, and zinc or cadmium-coated fasteners in wooden hulls. The whole subject of the corrosion of metals by wood receives detailed treatment in Section 18.10.

Lagging of process pipes can create similar trouble by absorbing moisture during shut-down periods or by becoming wet through atmospheric exposure or through condensation¹⁷. Certain lagging materials may also contain chloride ions. Calcium silicate is the preferred lagging material and moisture absorption should be prevented by the application of a waterproof coating to the insulation and/or ensuring that any trapped moisture may be subsequently ventilated. Process pipework should, of course, receive a properly applied, high quality and compatible coating system prior to application of insulation materials and thereafter be regularly inspected in service to ensure that no breakdown in the protective coating and insulation system has occurred, *otherwise exceedingly high corrosion rates may result*.

The other main cause of metals remaining wet under atmospheric conditions is condensation. This is particularly liable to occur in mess and pipe decks, laundries, galleys, machinery or piping areas or indeed in any enclosed space where humid conditions prevail. Such conditions also encourage the growth of bacteria and fungi which are not only a potential safety hazard but also a source of deterioration of paint coatings resulting in enhanced attack of metals due to the corrosive nature of their products of metabolism. Cadmium plating which is used extensively in electronic equipment and in the coating of fasteners is particularly vulnerable to this form of attack¹⁰. The cost-effective solution to condensation problems in enclosed spaces is often found to be air conditioning. If this is not practicable, then the use of dehumidifiers, the provision of as much ventilation as possible or vapour-phase inhibition (VPI) treatment should be considered. Care should also be taken to design or locate equipment in such a way that free circulation of preferably dry air is not impeded. Condensation, usually contaminated with chlorides, is also prone to occur on the external surfaces of marine structures in dry dock because of the humid conditions that often prevail in such locations.

Design considerations in relation to protective coating systems

A wide variety of protective coating types and systems is available for corrosion control on external and internal surfaces of structural and process plant in marine and offshore engineering. These are discussed in detail elsewhere in this text, and the purpose here is to highlight the critical importance of certain design and related operational aspects which affect both the selection and performance of protective coating systems. The following design considerations should be made:

1. Coatings should be applied to surfaces under the optimal possible environmental conditions. Shop-applied systems generally perform better than the same systems in field-applied situations. Monitoring and control of humidity and other application circumstances are critical in securing good results from high performance marine and offshore coatings.
2. Coatings should only be applied to fully and correctly prepared surfaces. Surface preparation is discussed elsewhere in this text; however, the following undesirable surface design/operational features should be eliminated wherever possible:
 - (a) excessive numbers of holes, sharp edges and rapid changes in section or surface profile;
 - (b) undressed welds, severe pitting or surface defects;
 - (c) risk of subsequent mechanical, electrical, chemical or welding damage to the coating;
 - (d) excessive temperatures or temperature range, frequency of temperature change (as may be found in process plant subject to thermal cycling);
 - (e) excessive changes in pressure (as may be found in certain intermittently-used subsea equipment, internals of hyperbaric chambers etc);
 - (f) areas of the coated surface which when in service, cannot be inspected (or maintained when necessary).

It may be that if one or other of the foregoing deficiencies exist, then other surface design changes or changes in corrosion control procedure should be considered.

Even if no deficiencies exist, it is important to realise at the design stage that if a protective coating system is to be used as part or whole means of corrosion control, there must be a 'downstream' commitment to inspection/maintenance/renewal of the coating system, as appropriate to the particular operating life of the coating system.

Seawater Systems

General Design and Layout

The conditions under which these systems operate can be extremely severe and, although the alloys at present available and in extensive use in sea-

water systems offer good resistance to many forms of attack, even the most resistant can fail under the conditions that can arise from poor design installation or operational detail. In fact, these systems provide an outstanding example of the important part that design can play in minimising corrosion and related conjoint degradation phenomena such as corrosion erosion.

The ideal design is one in which all parts can be operated satisfactorily with water flowing with the least turbulence and aeration, and at a rate of flow within the limits that the materials involved can securely withstand. These limits, with regard to flow-rate limitations, vary with the material, as described in Section 1.2, but turbulence, aeration or presence of suspended particulates can lower these limits considerably, and designs that eliminate these two factors go a long way towards preventing impingement attack, which can be the major cause of failures in sea-water systems. (See also Sections 1.6 and 2.1.)

Good designs should start at the inlets which should be shaped to produce smooth streamline flow with least turbulence and minimal ingress of deleterious substances. In the case of the ships' inlets they should be located in the hull in positions, so far as is practicable with other requirements, where turbulence is least excessive and the amount of entrained air is as low as possible. Inlets located close under the bilge keel or immediately aft of a pump discharge are in particularly bad positions. The design should not impart a rotatory motion to the water stream, since the vortex formed (in which air bubbles will tend to be drawn and cavitation problems induced) can travel along the piping until disrupted by some change in the geometry of the system, e.g. a bend or change of section in the piping or an irregularity in the bore. The energy will then be released resulting in an excessive local speed of highly aerated water and consequent rapid impingement and wall-thinning attack. Some reduction in the amount of air in the water stream can be achieved by the maximum use of air-release pipes and fittings.

To ensure that the water flows through the whole of the system as smoothly as possible and with the minimum of turbulence, it is vital that the layout of pipework should be planned before fabrication starts. It should not be the result of haphazard improvisation to avoid more and more obstacles as construction proceeds. Pipe runs should be minimised or run as directly as possible with every effort made to avoid features that might act as turbulence raisers. For this reason the number of flow controllers, process probes, bends, branches, valves, flanges, intrusive fittings, or mechanical deformation or damage to the pipework, should be kept to a minimum.

In some systems it may be feasible to select the sizes of pipes to give the correct speed in all branches without the need for flow-regulating devices, or a bypass may be satisfactory thereby eliminating one possible source of turbulence. Where flow control is necessary, this should be effected preferably either by valves of the glandless diaphragm type or by orifice plates, in either case set to pass the designed quantity of water under the conditions of maximum supply pressure normally encountered. Screw-down valves are not advised for throttling, nor are sluice and gate valves, as these in the partly open position cause severe turbulence with increased local speed and potentially serious erosion problems on the downstream side. For auxiliary heat exchangers and sanitary services in ships fed by water from the firemain

(which is at a high pressure), effective pressure-reducing valves must be fitted, otherwise rapid failures by impingement attack are almost inevitable. It is very important that all flow-regulating devices should be fitted only on the outlet side of equipment.

With regard to the various other features in a piping system that can set up turbulence, careful design of these can do much to reduce, if not completely eliminate, their harmful effects. Thus, pipe bends need cause little trouble if the radius of the bend is sufficiently large. A radius of four times the pipe diameter is a practice followed in some installations as well as by some authorities, with a relaxation to a radius of times three when space is restricted. Crimping of bends should be avoided by the use of a filler during bending, but care should be taken to remove all traces of filler residues before putting the pipe into service as these can initiate corrosion.

Branch pipes cause the minimum disturbance if they can be taken off the main piping by swept 'T' pieces rather than by right-angled junctions. Where the latter are unavoidable the diameter of the branch main should be as generous as possible. If connecting pieces are not used, branch pipes should be set at a shallow angle with the main piping and should not protrude into the latter.

Flanged joints are a very common cause of turbulence unless correctly made and fitted. Close tolerances should be placed on the machining of flanges to match the bore of the pipe; mating flanges should be parallel and correctly aligned, and gaskets should be fitted so that they are flush with the bore and do not protrude into the pipe. Alternatively, butt welding can be used provided pipe ends are not misaligned and weld metal roots do not protrude into the bore. Screwed union fittings also give no trouble if pipes are correctly aligned. A further precaution to lessen the risk of impingement attack is to fit straight lengths of pipe down-stream of possible turbulence raisers.

Piping Materials

The characteristics of the various metals commonly used for seawater systems, chiefly, nickel and titanium alloys, galvanised steel and to a lesser extent aluminium alloys and stainless steels, are fully described in their respective sections. Reference here will be confined to mentioning some of the advantages and limitations of clad and non-metallic piping.

As regards the former, a recent development has been the cladding of steel piping with a welded overlay of cupro-nickel which shows promising application for components such as ships' inlet trunking. Non-metallic-clad steel piping, if correctly manufactured and fitted, has the advantage of being resistant to deterioration by seawater at the speeds normally encountered. However, if the coatings possess pin-holes or other discontinuities or are too brittle to withstand a reasonable amount of shock or are damaged by subsequent welding or cutting operations, water may gain access to the steel causing rapid perforation or lifting of the coating and corrosion of the pipe walls with the possibility of a blockage ensuing.

Non-metallic materials can provide cost-effective and secure solutions

to many corrosion problems in the marine and offshore industries. They can be used as corrosion-resistant lining materials or as piping materials in their own right. In particular, glass fibre reinforced plastic (GFRP) and glass fibre reinforced epoxy (GFRE) materials have been the subjects of sustained development work. GFRP has been successfully developed for both structural and process applications, such as the hulls of minesweepers and low-pressure secondary pipework applications. GFRE, on the other hand, is largely a product of the space age, being used originally for rocket-motor cases and even today is used on Polaris and Minuteman class rockets and solid-booster motors for the space shuttle. GFRE has been mainly developed for process applications and indeed was used originally for oilfield pipework in the 1950s. Later applications include flow lines and gathering lines, secondary-recovery waterflood systems and, in the 1970s, downhole tubing and casing at depths to 3 000 m. In recent years, the American Petroleum Institute (API) has introduced specifications for GFRP and GFRE line pipe materials, namely API 15LR for low pressure line pipe (<1 000 psi) and API 15HR for high pressure line pipe (>1 000 psi). An interesting specification has also been produced for downhole tubing and casing (API 15AR) which is due for further review¹⁸.

GFRP and GFRE materials have very good general corrosion resistance in a wide variety of marine and offshore process media. In addition, they are lightweight (being only 10–25% as dense as steel), strong, non-magnetic, and are now widely available at reasonable cost. Fabrication and assembly of pipework systems can be easily achieved by bell-and-spigot glued joints or by other commercially-available mechanical jointing systems. The principal limitations of these materials remain in terms of their relatively poor fire and mechanical damage resistance, restricted size range availability and certain mechanical and chemical property shortcomings. In addition, assembly and installational detail of pipework has to be carefully undertaken to ensure that no installational or in-service damage (such as distortion or sagging) is sustained.

Nevertheless, it is clear that these materials should form an increasingly important range of corrosion-resisting materials for use in marine and offshore pipework and vessels in the years ahead.

Design of Components and Fittings

Even with the velocity, turbulence and aeration of the water supplied to the equipment being within acceptable limits, if corrosion is to be avoided it is still necessary for the units themselves to be well designed. Some of the more important aspects involved are outlined below.

Condensers, heat exchangers and process coolers The shape of the inlet water box and the shape and positioning of the entry should be designed to produce as smooth a flow of water as possible, evenly distributed over the tubeplate. Poor design can result in high-speed turbulent water regimes developing at certain points, which may give rise to cavitation and impingement conditions at some areas of the tubeplate and particularly at some

tube ends; in other relatively stagnant pockets some tubes may receive an inadequate supply of water, leading to overheating or to the settlement of debris, with consequent deposit attack.

Non-condensing gases can also accumulate in a stagnant area accentuating the tendency to local overheating, but this can be counteracted to some extent by the provision of adequate air-escape fittings. Local overheating may also be caused by impingement of steam due to poor baffling, and this can cause penetration of the tubes by wet steam erosion. Local overheating of Cu-30Ni cupronickel tubes may lead to 'hot spot' corrosion^{11,12}. More general overheating, which can occur with some auxiliary condensers, particularly drain coolers, may cause a rapid build-up of scale on the inside of the tubes necessitating acid descaling.

Design faults in two-pass condensers and heat exchangers that can cause corrosion include poor division plate seals allowing the escape of water at high velocity between the passes, and flow patterns that produce stagnant zones.

Partial blockages of tubes by debris can act as turbulence raisers and should be guarded against by fitting either weed grids, filters or plastic inserts in the tube ends so that any object passing through the insert is unlikely to become jammed in the tube. These methods will not, however, prevent trouble from marine organisms that enter the system in their early stages of development. This can usually be effectively dealt with by intermittent chlorination or by other chemical dosing treatment. An alternative scheme is to fill the system with fresh water for a period, followed by removal of the dead organisms by water jetting or by an approved mechanical method. Marine organisms dislike changes in conditions such as water salinity, temperature, flow rate, etc.

An important point in the design of condensers and heat exchangers is the provision of facilities that allow ready access for cleaning and maintenance. Access doors should be well sited and should be clear of pipework and fittings. Covers of smaller heat exchangers should be easy to remove well clear of the units. Small doors should be fitted at the lowest point to enable residual fluid and debris to be flushed out, thus ensuring complete drainage when this is required. Lack of these facilities understandably tends to result in maintenance procedures not being carried out as frequently or as well as they should, and this can lead to serious corrosion problems which may be insoluble in the particular plant location.

The final point to be mentioned on the subject of marine condenser, heat exchanger or process cooler design is the danger of purchasing auxiliary units through 'package deals', which may be adequate for fresh-water service but can have an extremely limited life when operated on seawater. In addition, equipment designed for use on land even for seawater service often proves unsatisfactory when installed in ships or offshore installations. It is generally preferable for such equipment to be specifically designed for the purposes intended.

Pumps and valves In addition to designing these so as to cause least turbulence in the water stream, careful design can also minimise corrosion of the pumps and valves themselves.

Pumps can be a major source of trouble, with rapid deterioration of parts due to impingement, cavitation or galvanic corrosion problems¹³. The latter two issues may be the result of either poor design or exacerbated by the conditions under which the pump is operated. The remedy may be found in changes in material, since some materials resist cavitation better than others. However, even the most resistant material may have a short life if the cavitation is severe. Designs should avoid features that produce excessive turbulence which may induce cavitation, or that allow the passage of high-velocity water between the high- and low-pressure areas. Cavitation in pumps can develop if the water supply is not continuous, e.g. when pumping-out bilges, especially with choked strainers or lines, or if the water supply is controlled by a badly designed throttling device. Pumps with high suction heads are particularly prone to suffer cavitation damage. Conditions in pumps can still be severe, however, in the absence of cavitation, and high duty materials may be necessary for a reasonable service life. The use of silastomer or neoprene coatings and linings can often give good results even in reasonably severe service conditions.

As regards valves, diaphragm types are the most satisfactory but most valves have to withstand extremely turbulent conditions, and as with pumps, even the best designs need to be constructed of resistant materials, or be coated with a suitably durable material such as silastomer or neoprene.

Designs to Prevent Galvanic Corrosion

In general it is wise to avoid as far as possible, the use of incompatible metallic joints in marine and offshore practice, since these are often in contact with seawater or water that contains chlorides which are effective corrosive electrolytes. It is prudent to take very considerable precautions to prevent corrosion at the design and installational stages. However, the widely diverse properties required of the materials used in such installations make it impracticable to avoid all such joints.

In seawater systems contact between metals and alloys with differing corrosion potentials* is very common. Recurrent difficulties may be faced with anodic welded joint areas, for example¹⁴. Internal lining, material or procedural changes are often the only methods of dealing effectively with the problem. In condensers, iron protector slabs can be employed, although ferrous water boxes sometimes serve the same purpose; impressed-current cathodic protection systems are also finding extended use. Different alloys are also to be found in contact in valves, pumps and other equipment, and between these components and copper-alloy piping; these seldom have closely similar corrosion potentials, but many can have only slight differences that are of little consequence in practice. Even where components have a significant difference in potential, this can often be acceptable if the less noble component is large in area compared with the more noble metal,

*The reversible or equilibrium potentials given in the EMF series of metals may have little significance in assessing which metal in a couple will have an enhanced corrosion rate and which will be protected.

or is of thicker section and can be allowed to suffer a certain amount of corrosion loss without effect on overall plant integrity. In fact, the galvanic sacrificial protection afforded by this means to a more noble and vital component can be most valuable, as for example if pump impellers are given some protection by the pump casing which is often of a ferrous material such as cast iron. The tendency for some otherwise highly corrosion-resistant alloys to suffer crevice attack can also often be overcome in this way.

Other combinations, however, do create difficulties. For example, non-ferrous components and fittings such as copper-alloy valves and sea-tubes can cause serious corrosion of adjacent steel, the galvanic attack in many of these instances being accentuated by crevicing, high water speeds and sometimes by the inadequate design of inlets which promote turbulence and contribute to the difficulty of maintaining paint films intact for any length of time. It should be noted that the extent and rate of damage is also dependent on the area ratio of the cathode to anode areas of the two metals, and this is a maximum when a large cathode area is acting on a small anode area.

Corrosion in these areas is sometimes effectively controlled by cathodic protection with zinc- or aluminium-alloy sacrificial anodes in the form of a ring fixed in good electrical contact with the steel adjacent to the non-ferrous component. This often proves only partially successful, however, and it also presents a possible danger since the corrosion of the anode may allow pieces to become detached which can damage the main circulating-pump impeller. Cladding by corrosion-resistant overlays such as cupronickel or nickel-base alloys may be an effective solution in difficult installational circumstances.

Non-ferrous propellers in ships can cause similar trouble, especially during the ship's fitting-out period. This may be controlled by not fitting the propellers until the final dry docking prior to carrying out sea trials; by coating the propellers prior to launching and removing the coating at the final dry docking; and by cathodic protection of the whole outer bottom. The protection of the outboard propeller shaft is most successfully achieved by a coating of epoxy resin reinforced with glass cloth. The earthing of shafts to the hull is advocated by some ship owners and by some navies, but the practical difficulties involved in maintaining good contact are substantial.

One of the most important and extensive applications of two metals in proximity in ship construction is the use of aluminium-alloy superstructures with steel hulls. This practice is now widely accepted in both naval and merchant services. The increased initial cost is more than offset by certain fabrication advantages, weight saving and fuel consumption, with the concomitant advantages of increased accommodation, a lowered centre of gravity giving greater stability (which is especially valuable for ships carrying deck cargo) and a lighter draft. These advantages are so substantial that the use of these two metals in juxtaposition even in a marine environment must be accepted. Serious trouble can, however, usually be avoided if the following steps are taken:

1. The metal interface should be designed to be as high a quality fit as possible.

2. The faying surface of the steel should be given a metal coating of either zinc (by spraying or galvanising) or aluminium spray.
3. Jointing compounds such as neoprene tape or fabric strip impregnated with chromate inhibitor or other inhibited caulking compounds should be applied carefully to ensure complete exclusion of water.
4. Rivets or other forms of fastenings should be of a similar material to the plate with which it is in contact.
5. The joint should be painted on both sides with the appropriate coating systems (following a suitable surface preparation programme).

Regardless of the method selected, great attention must nevertheless be given to ensuring that the final detail is sound and able to be inspected and repaired if necessary, when the structure is in service.

Galvanic corrosion arising from different metals not in 'direct' electrical contact must also be guarded against. In particular, water containing small amounts of copper resulting from condensation, leakage or actual discharge from copper and copper-alloy pipes and fittings, can cause accelerated attack of steel plating with which it comes into contact. Likewise copper pipes carrying iron or steel particles may also suffer pitting attack as a consequence of microgalvanic cells created by such particles forming wall contacts. Good design and 'clean' operating practices can help prevent this. In addition, both the pipework and the plating should be accessible for inspection and for applying and maintaining protective coatings.

Stress-corrosion Cracking, Corrosion Fatigue and Cavitation Damage

Some examples of how design can assist in counteracting these forms of attack in marine and offshore practice are given below. The three phenomena are dealt with comprehensively in Chapter 8.

Stress corrosion cracking

Low-carbon and chromium-nickel steels, certain copper, nickel and aluminium alloys (which are all widely used in marine and offshore engineering) are liable to exhibit stress-corrosion cracking whilst in service in specific environments, where combinations of perhaps relatively modest stress levels in material exposed to environments which are wet, damp or humid, and in the presence of certain gases or ions such as oxygen, chlorides, nitrates, hydroxides, chromates, nitrates, sulphides, sulphates, etc.

A broad indication of the principal environmental features which may promote stress-corrosion cracking is given in Table 9.4¹⁵. The list is by no means exhaustive but it is useful in preliminary stress-corrosion cracking risk assessment within the design process. In addition, the temperature of the environment may also be a contributory factor in stress-corrosion cracking processes. Consequently, the high-risk areas will include boilers, heat exchangers, process coolers, drilling equipment, downhole tubulars, wireline

Table 9.4 Environments known to promote stress-corrosion cracking in certain engineering alloys¹⁵

<i>Material</i>	<i>Environments</i>
Al alloys	Chlorides, moist air
Mg alloys	Chloride-chromate mixtures, moist air, nitric acid, fluorides, sodium hydroxide
Cu alloys	Ammonia, moist air, moist sulphur dioxide
C steels	Nitrates, hydroxides, carbonates, anhydrous ammonia
Austenitic steels	Chlorides, sulphuric acid
High strength steels	Moist air, water, chlorides, sulphates, sulphides
Ni alloys	Hydroxides
Ti alloys	Halides, methanol

and logging equipment, packers, wellhead and downstream oil and gas processing equipment.

Clearly, the lowering of stress-corrosion cracking risk at the design stage must be an important priority when dealing with the combinations of operational and environmental circumstances outlined above. It has become something of an increasing priority in recent years owing to the fact that certain engineering design trends or priorities—such as increasing strength/weight ratios—often lead to selection of higher alloy steels being used in highly stressed corrosive situations. In addition, there is a trend for certain industrial processes to be undertaken at progressively higher process temperatures, for example deeper (hence hotter) sour oil and gas wells being drilled and produced gives rise to increasing instances of chloride stress cracking (CSC) problems in oilfield equipment¹⁶.

An outline of the general design options for reduction of stress-corrosion cracking risk in marine and offshore installations can be summarised as follows:

1. Attempt to ensure that residual and operational tensile or oscillatory tensile (fatigue) stresses in components are kept moderate so far as reasonably practicable.
2. Provide effective means of corrosion protection of components consistent with operational circumstances. This may involve cathodic protection, inhibition, coatings or combinations of these.
3. Remove significant environmental influences as soon as reasonably practicable, e.g. dewatering/dehumidification of produced oils and gases as close to wellhead as possible.
4. Choose a material known to have reasonable and reliable intrinsic stress-corrosion cracking resistance in the operational media. For example, a very high stress-corrosion cracking risk would be attached to the installation of a highly stressed titanium-nickel cryogenic memory-alloy pipe coupling, used in the transmission of commercial-grade methanol (which may contain ca. 2 000 ppm water) for oil well dewaxing operations.
5. Ensure stress-raising features such as holes, welds, edges, rapid changes in section, etc, are minimised in their exposure to the stress-corrosion cracking risk environment. Heat treatment of components may give beneficial results.

Corrosion fatigue

Marine and offshore engineering, by its very nature involving many components being subjected to oscillating stress levels in a wide variety of aggressive media, has to consider corrosion fatigue as a serious risk in many instances. Again, the influences of water, dissolved oxygen, chlorides, etc., are all known to have generally deleterious effects on the corrosion fatigue performance of many engineering alloys¹⁵. Successful methods of counteraction may involve modification to the corrosive environment, reduction of fatigue stress levels by one means or another, corrosion protection or materials uprating. Recurrent high-risk corrosion fatigue areas, however, should be closely monitored. These areas include:

1. high-speed ship hull plates;
2. boiler and pipework components subject to pulsating stresses of thermal or mechanical origin;
3. condenser and heat exchanger tubing, where inadequate support/clamping arrangements are made;
4. propeller, impeller and pump shafts, connecting rods of diesel engines, gas turbine and gearbox components where intake air or oil is contaminated;
5. sucker rods in corrosive wells.

Many of the design rules applying to stress-corrosion cracking may also be considered as being potentially useful in minimising corrosion fatigue risk. Perhaps one area where cathodic protection should be applied with great caution is in circumstances where over-protection of a structure may give hydrogen evolution, which in turn may lead to hydrogen absorption of a component—particularly bolt, stud or shaft materials—which, in turn, may raise the risk of corrosion fatigue in certain marine and offshore installational circumstances.

Cavitation Damage

This type of damage is dealt with comprehensively in Section 8.8. It can be particularly severe in seawater giving rise to cavitation corrosion or cavitation erosion mechanisms, and hence can be a considerable problem in marine and offshore engineering. Components that may suffer in this way include the suction faces of propellers, the suction areas of pump impellers and casings, diffusers, shaft brackets, rudders and diesel-engine cylinder liners. There is also evidence that cavitation conditions can develop in seawater, drilling mud and produced oil/gas waterlines with turbulent high rates of flow.

Improvements in design that can assist in preventing cavitation damage may be concerned with the shape of the component itself, or with its surroundings. The design of propellers and impellers depends largely on the expertise of the manufacturers of these components. Where cavitation damage develops, this may occasionally be due to unsuitable design in relation to the conditions of service, but in most cases occurring in seawater systems, the trouble arises from other causes such as poor layout, air leaks

in suction piping or faulty operation. Underwater fittings should be designed to offer as little resistance as possible to movement through the water and to leave the minimum turbulence in their wake which might result in cavitation damage to other parts of the ship. Cathodic protection often proves of benefit in reducing damage to ships' propellers and underwater fittings. In addition, certain energy-absorbing coatings may effectively limit cavitation damage in pump casings, etc.

The geometry of piping systems, accuracy of fit, smoothness of internal surface, presence of turbulence creators etc., may be important contributory factors in instances of cavitation attack. Figure 9.24 shows cavitation erosion attack in tubing pulled from an oil and gas production well. The source of the cavitation attack was a downhole valve which produced severe downstream turbulence, even in the fully-open position. Such forms of attack, in lines where flow velocities may be as high as 100 m/s, may quickly become cumulative, producing further secondary or tertiary erosion bands downstream of the first area of attack. Internal coatings such as baked phenolics may be practical in some circumstances both from the corrosion control and 'surface smoothing' points of view.

Other design issues which may be considered when attempting to minimise cavitation damage include:

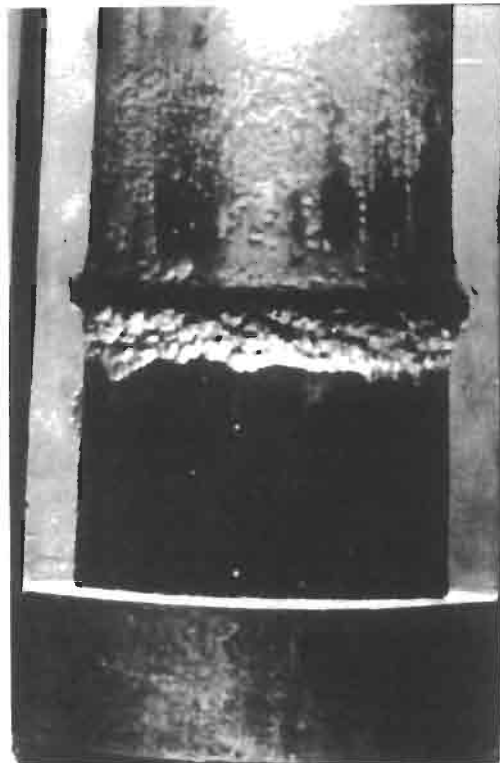


Fig. 9.24 Cavitation erosion in oil and gas production well tubing. Note the severe localised attack arising from a turbulence-creating downhole valve a few metres upstream

1. Improve quality of fit of pipe butts, flange areas, etc., to minimise weld root or gasket intrusion into the process flow, which may create cavitation damage.
2. Examine geometry and size of piping/flowline systems to ensure process streams are subject to minimal pressure changes and fluctuations, changes in fluid direction and flow rates consistent with production requirements.
3. Examine pressure heads and maximise whenever reasonably practicable to minimise vapour cavity formation.
4. Establish corrosivity levels of process streams and choose materials and protection systems appropriately.
5. If possible, cool process streams to minimise vapour cavity formation.

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9.5 Design in Relation to Welding and Joining

A jointed fabrication* is one in which two or more components are held in position (a) by means of a mechanical fastener (screw, rivet or bolt), (b) by welding, brazing or soldering or (c) by an adhesive. The components of the joint may be metals of similar or dissimilar composition and structure, metals and non-metals or they may be wholly non-metallic. Since the majority of fabrications are joined at some stage of their manufacture, the corrosion behaviour of joints is of the utmost importance, and the nature of the metals involved in the joint and the geometry of the joint may lead to a situation in which one of the metals is subjected to accelerated and localised attack. Although corrosion at bimetallic contacts involving different metals has been dealt with in Section 1.7, it is necessary to emphasise the following in relation to corrosion at joints in which the metals involved may be either identical or similar:

1. A difference in potential may result from differences in structure or stress brought about during or subsequent to the joining process.
2. Large differences in area may exist in certain jointed structures, e.g. when fastening is used.

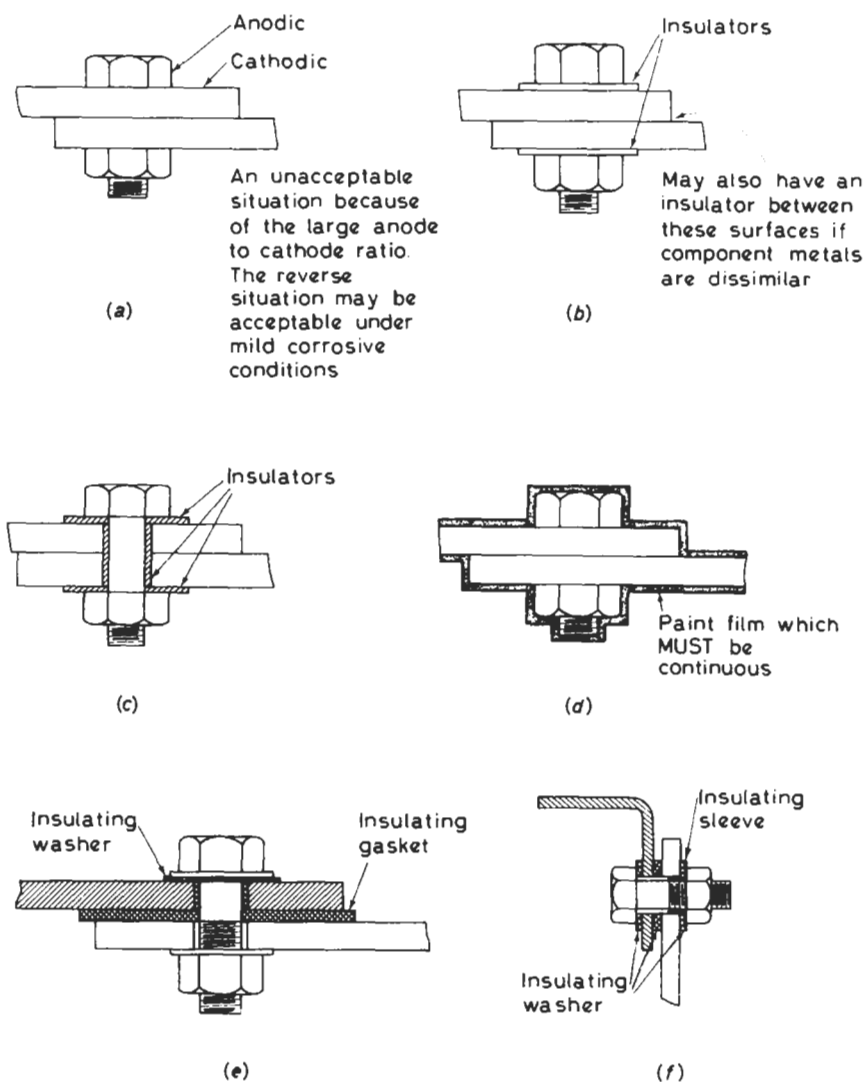
Furthermore, many joining processes lead to a crevice, with the consequent possibility of crevice corrosion.

Before considering the factors that lead to corrosion it is necessary to examine briefly the basic operations of joint manufacture.

Mechanical Fasteners

These require little description and take the form of boltings, screws, rivets, etc. Mechanical failure may occur as a result of the applied stress in shear or tension exceeding the ultimate strength of the fastener, and can normally be ascribed to poor design, although the possibility of the failure of steel fittings at ambient or sub-zero temperatures by brittle fracture, or at ambient temperatures by hydrogen embrittlement, cannot be ignored. If brittle failure is a problem then it can be overcome by changing the joint design or

* For definitions of terms used in this section see Section 9.5A.

Fig. 9.25 Design of insulated joints⁵

employing a fastener having a composition with better ductility transition properties.

The corrosion problems associated with mechanical fixtures are often one of two types, i.e. crevice corrosion or bimetallic corrosion¹⁻⁴, which have been dealt with in some detail in Sections 1.6 and 1.7, respectively.

The mechanical joining of aluminium alloys to steels using rivets and bolts, a combination which is difficult to avoid in the shipbuilding industry, represents a typical example of a situation where subsequent bimetallic corrosion could occur. Similarly, other examples of an ill-conceived choice of materials, which could normally be avoided, can be found in, for

example, brass screws to attach aluminium plates or steel pins in the hinges of aluminium windows.

The relative areas of the metals being joined is of primary importance in bimetallic corrosion, and for example, stainless steel rivets can be used to joint aluminium sheet, whereas the reverse situation would lead to rapid deterioration of aluminium rivets. However, in the former case a dangerous situation could arise if a crevice was present, e.g. a loose rivet, since under these circumstances the effective anodic area of the aluminium sheet would be reduced, with consequent localised attack. In general, under severe environmental conditions it is always necessary to insulate the components from each other by use of insulating washers, sleeves, gaskets, etc. (Fig. 9.25)⁵, and the greater the danger of bimetallic corrosion the greater the necessity to ensure complete insulation; washers may suffice under mild conditions but a sleeve must be used additionally when the conditions are severe.

The fasteners themselves may be protected from corrosion and made compatible with the metal to be fastened by the use of a suitable protective coating, e.g. metallic coating, paints, conversion coating, etc. The choice of fastener and protective coating, or the material from which it is manufactured, must be made in relation to the components of the joint and environmental conditions prevailing⁶. Thus high-strength steels used for fastening the fuselage of aircraft are cadmium plated to protect the steel and to provide a coating that is compatible with the aluminium. In the case of protection with paints it is dangerous to confine the paint to the more anodic component of the joint, since if the paint is scratched intense localised attack is likely to occur on the exposed metal.

In general, paint coatings should be applied to both the anodic and cathodic metal, but if this is not possible the more cathodic metal rather than the more anodic metal should be painted. The use of high-strength steels for bolts for fastening mild steel does not normally present problems, but a serious situation could arise if the structure is to be cathodically protected, particularly if a power-impressed system is used, since failure could then occur by hydrogen embrittlement; in general, the higher the strength of the steel and the higher the stress the greater the susceptibility to cracking.

A point that cannot be overemphasised is that, in the long term, stainless steel fasteners should be used for securing joints of stainless steel.

Soldered Joints

Soldering and brazing are methods of joining components together with a lower-melting-point alloy so that the parent metal (the metal or metals to be joined) is not melted (Table 9.5). In the case of soft soldering the maximum temperature employed is usually of the order of 250°C and the filler alloys (used for joining) are generally based on the tin-lead system. The components must present a clean surface to the solder to allow efficient wetting and flow of the molten filler and to provide a joint of adequate mechanical strength. To obtain the necessary cleanliness, degreasing and mechanical abrasion may be required followed by the use of a flux to remove any

Table 9.5 Soldering and brazing

<i>Process</i>	<i>Temp. range (°C)</i>	<i>Typical fillers</i>	<i>Fluxes</i>
SOLDERING			
hot iron	60–300	70Pb–30Sn	Chloride based Fluoride based Resin based
oven		40Pb–60Sn	
induction		70Pb–27Sn–3Sb	
ultrasonic		40Pb–58Sn–2Sb	
dip		Sn–Zn–Pb	
resistance			
wave and cascade			
BRAZING			
torch	500–1 200	90Al–10Si	Borax based Fluoride based Hydrogen gas Town's gas Vacuum
dip		50Ag–15Cu–17Zn–18Cd	
salt bath		Ag–Cu–Ni–In	
furnace		60Ag–30Cu–10Zn	
induction		50Cu–50Zn	
resistance		97Cu–3P	
		70Ni–17Cr–3B–10Fe	
		82Ni–7Cr–5Si–3Fe	
		60Pd–40Ni	

remaining oxide film and to ensure that no tarnish film develops on subsequent heating.

In the case of carbon steels and stainless steels, and many of the non-ferrous alloys, the fluxes are based on acidic inorganic salts, e.g. chlorides, which are highly corrosive to the metal unless they are removed subsequently by washing in hot water. For soldering tinsplate, clean copper and brass, it is possible to formulate resin-based fluxes having non-corrosive residues and these are essential for all electrical and electronic work. Activators are added to the resin to increase the reaction rate, but these must be such that they are thermally decomposed at the soldering temperature if subsequent corrosion is to be avoided⁷. Corrosion is always a risk with soldered joints in aluminium owing to the difference in electrical potential between the filler alloy and the parent metal and the highly corrosive nature of the flux that is generally used for soldering. However, it is possible to employ ultrasonic soldering to eliminate use of flux. With aluminium soldering it is imperative that the joints be well cleaned both prior and subsequent to the soldering operation, and the design should avoid subsequent trapping of moisture.

Brazed Joints

When stronger joints are required, brazing may be used⁸. The filler alloys employed generally melt at much higher temperatures (600–1 200°C), but the effectiveness of the joining process still depends upon surface cleanliness of the components to ensure adequate wetting and spreading. Metallurgical and mechanical hazards may be encountered in that the filler may show poor spreading or joint filling capacity in a certain situation

or may suffer from hot tearing, whilst during furnace brazing in hydrogen-containing atmospheres there is always the possibility that the parent metal may be susceptible to hydrogen embrittlement or steam cracking. Furthermore, brittle diffusion products may be produced at the filler base-metal interface as a result of the reaction of a component of the filler alloy with a base-metal component, e.g. phosphorus-bearing fillers used for steel in which the phosphorus diffuses into the steel.

Serious damage can be caused by (a) diffusion into the parent metal of the molten brazing alloy itself when either one or both of the parent metal(s) is in a stressed condition induced by previous heat treatment or cold working, and (b) by an externally applied load which need only be the weight of the workpiece. Nickel and nickel-rich alloys are particularly prone to liquid-braze-filler attack especially when using silver-based braze fillers at temperatures well below the annealing temperature of the base metal, since under these conditions there is then no adequate stress relief of the parent metal at the brazing temperature. The problem may be avoided by annealing prior to brazing and ensuring the maintenance of stress-free conditions throughout the brazing cycle. There is a whole range of silver-, nickel- and palladium-based braze fillers of high oxidation and corrosion resistance that have been developed for joining the nickel-rich alloys; however, the presence of sulphur, lead or phosphorus in the base-metal surface or in the filler can be harmful, since quite small amounts can lead to interface embrittlement (Section 7.5). In the case of the Monels, the corrosion resistance of the joint is generally less than that of the parent metal and the design must be such that as little as possible of the joint is exposed to the corrosive media.

When, in an engineering structure, the aluminium-bronzes are used for their corrosion resistance, the selection of braze filler becomes important and although the copper-zinc brazing alloys are widely used, the corrosion resistance of the joint will be that of the equivalent brass rather than that of the bronze. With the carbon and low-alloy steels, the braze fillers are invariably noble to the steel so that there is little likelihood of trouble (small cathode/large anode system), but for stainless steels a high-silver braze filler alloy is desirable for retaining the corrosion resistance of the joint, although stress-corrosion cracking of the filler is always a possibility if the latter contains any zinc, cadmium or tin.

An interesting example of judicious choice of braze filler is to be found in the selection of silver alloys for the brazing of stainless steels to be subsequently used in a tap-water environment⁹. Although the brazed joint may appear to be quite satisfactory, after a relatively short exposure period failure of the joint occurs by a mechanism which appears to be due to the break-down of the bond between the filler and the base metal. Dezincification is a prominent feature of the phenomenon¹⁰ and zinc-free braze alloys based on the Ag-Cu system with the addition of nickel and tin have been found to inhibit this form of attack. A similar result is obtained by electroplating 0.007 mm of nickel over the joint area prior to brazing with a more conventional Ag-Cu-Zn-Cd alloy.

Brazing is generally considered unsuitable for equipment exposed to ammonia and various ammoniacal solutions because of the aggressiveness of ammonia to copper- and nickel-base alloys, but recently an alloy based

Table 9.6 Typical joining processes

<i>Joining process</i>	<i>Types</i>
Mechanical fasteners	Nuts, bolts, rivets, screws
Soldering and brazing	Hot iron, torch, furnace, vacuum
Fusion welding	Oxyacetylene, manual metal arc, tungsten inert gas, metal inert gas, carbon dioxide, pulsed arc, fused arc, submerged arc, electro slag and electron beam
Resistance welding	Spot, seam, stitch, projection, butt and flash butt
Solid-phase welding	Pressure, friction, ultrasonic and explosive

on Fe-3·25B-4·40Si-50·25Ni has been shown to be suitable for such applications¹¹.

Upton¹² has recently studied the marine corrosion behaviour of a number of braze alloy-parent metal combinations and has shown that compatibility was a function of the compositions of the filler and parent metals, their micro-structures and chance factors such as overheating during the brazing operation.

Welded Joints

The welded joint differs from all others in that an attempt is made to produce a continuity of homogeneous material which may or may not involve the incorporation of a filler material. There are a large variety of processes by which this may be achieved, most of which depend upon the application of thermal energy to bring about a plastic or molten state of the metal surfaces to be joined. The more common processes used are classified in Table 9.6.

The macrographic examination of a welded joint shows two distinct zones, namely the fusion zone with its immediate surroundings and the parent metal (Fig. 9.26). It is apparent therefore, that such processes produce differences in microstructure between the cast deposit, the heat-affected zone which has undergone a variety of thermal cycles, and the parent plate. Furthermore, differences in chemical composition can be introduced accidentally (burnout of alloying elements) or deliberately (dissimilar metal joint). Other characteristics of welding include: (1) the production of a residual stress system which remains after welding is completed, and which, in the vicinity of the weld, is tensile and can attain a magnitude up to the yield point; (2) in the case of fusion welding the surface of the deposited metal is rough owing to the presence of a ripple which is both a stress raiser and a site for the condensation of moisture; (3) the joint area is covered with an oxide scale and possibly a slag deposit which may be chemically reactive, particularly if hygroscopic; and (4) protective coatings on the metals to be joined are burnt off so that the weld and the parent metal in its vicinity become unprotected compared with the bulk of the plate.

Therefore, the use of welding as a method of fabrication may modify the corrosion behaviour of an engineering structure, and this may be further aggravated by removal of protective systems applied before welding, whilst at the same time the use of such anti-corrosion coatings may lead to difficulties in obtaining satisfactorily welded joints¹³⁻¹⁶.

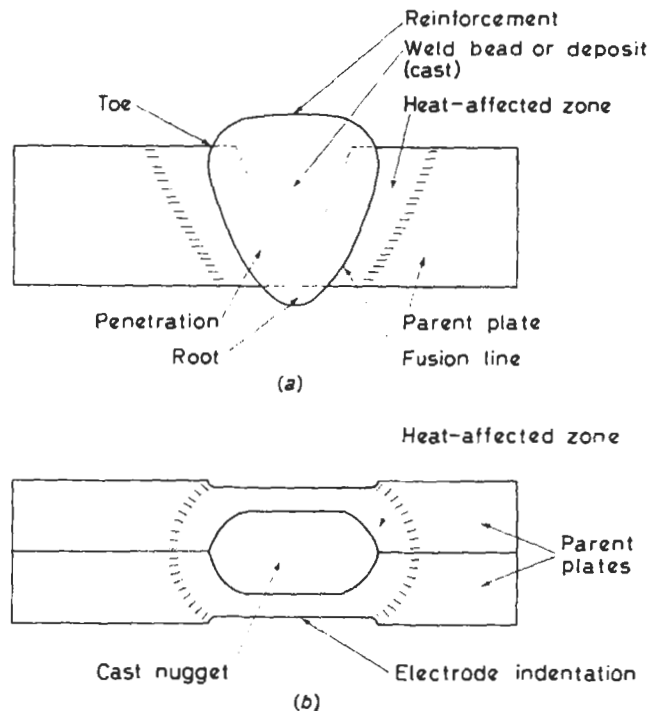


Fig. 9.26 Weld definitions. (a) Fusion weld and (b) resistance spot weld

Weld Defects

There is no guarantee that crack-free joints will automatically be obtained when fabricating 'weldable' metals. This is a result of the fact that weldability is not a specific material property but a combination of the properties of the parent metals, filler metal (if used) and various other factors (Table 9.7)¹⁷. The consequence of the average structural material possessing imperfect weldability is to produce a situation where defects may arise in the weld deposit or heat-affected zone (Table 9.8 and Fig. 9.27).

It is obvious that these physical defects are dangerous in their own right but it is also possible for them to lead to subsequent corrosion problems, e.g. pitting corrosion at superficial non-metallic inclusions and crevice corrosion at pores or cracks. Other weld irregularities which may give rise to crevices include the joint angle, the presence of backing strips and spatter (Fig. 9.29). Butt welds are to be preferred since these produce a crevice-free profile and, furthermore, allow ready removal of corrosive fluxes.

Carbon and Low-alloy Steels

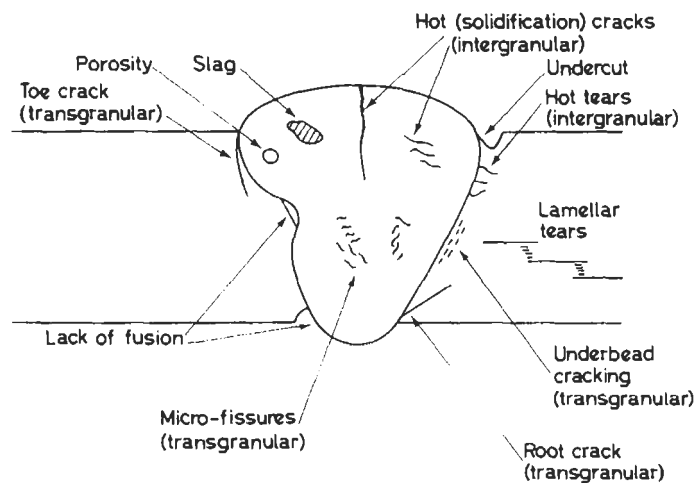
These usually present little problem since the parent and filler metals are generally of similar composition, although there is some evidence that the

Table 9.7 Factors affecting weldability*

<i>Parent metal</i>	<i>Filler metal</i>	<i>Other factors</i>
Composition Thickness State of heat treatment Toughness Temperature Purity Homogeneity	Composition Impact strength Toughness Hydrogen content Purity Homogeneity Electrode diameter (Heat input during welding)	Degree of fusion (Joint formation) Degree of restraint Form factor (Transitions) Deposition technique Skill and reliability of the welder

*Data after Lundin¹⁷**Table 9.8** Weldability defects

<i>Defect</i>	<i>Causes</i>	<i>Remedies</i>
Hot cracks	Large solidification range Segregation Stress	More crack-proof filler Less fusion
Underbead cracks	Hardenable parent plate Hydrogen Stress	Low hydrogen process Planned bead sequence Preheating
Microfissures	Hardenable deposit Hydrogen Stress	Low hydrogen process Pre- and post-heating
Toe cracks	High stress Notches Hardenable parent plate	Planned bead sequence Preheating Avoidance of notches
Hot tears	Segregation Stress	Less fusion Cleaner parent plate
Porosity	Gas absorption	Remove surface scale Remove surface moisture Cleaner gas shield

**Fig. 9.27** Possible weld defects

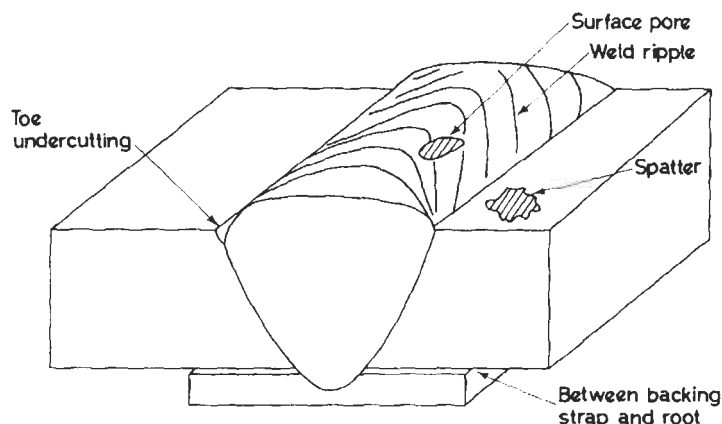


Fig. 9.28 Possible crevice sites

precise electrode type in manual metal-arc welding for marine conditions may be important; weld metal deposited from basic-coated rods appears to corrode more rapidly than that deposited from rutile-based coatings¹⁸.

An environment containing H_2S , cyanides, nitrates or alkalis may produce stress-corrosion cracking in highly stressed structures and these should be first stress relieved by heating to $650^\circ C$.

An interesting development in weldable corrosion-resistant steels is the copper-bearing or weathering steels (Section 3.2) which exhibit enhanced corrosion resistance in industrial atmospheres in the unpainted condition. For optimum corrosion resistance after welding, the filler employed should be suitably alloyed to give a deposit of composition similar to that of the steel plate¹⁹.

Stainless Irons and Steels

Since stainless irons and steels (Section 3.3) are widely used for resisting corrosive environments, it is relevant to consider the welding of these alloys in some detail. There are three groups of stainless steels, each possessing their own characteristic welding problem:

1. Ferritic type. Welding produces a brittle deposit and a brittle heat-affected zone caused by the very large grain size that is produced. The problem may be reduced in severity by the use of austenitic fillers and/or the application of pre- and post-weld heat treatments; the latter is a serious limitation when large welded structures are involved.
2. Martensitic type. Heat-affected zone cracking is likely and may be remedied by employing the normal measures required for the control of hydrogen-induced cracking.
3. Austenitic types. These are susceptible to hot cracking which may be overcome by balancing the weld metal composition to allow the formation of a small amount of δ -Fe (ferrite) in the deposit, optimum crack resistance being achieved with a δ -Fe content of 5–10%. More than

this concentration increases the possibility of σ -phase formation if the weldment is used at elevated temperature with a concomitant reduction in both mechanical and corrosion properties.

The corrosion of stainless steel welds has probably been studied more fully than any other form of joint corrosion and the field has been well reviewed by Pinnow and Moskowitz²⁰, whilst extensive interest is currently being shown by workers at The Welding Institute²¹. Satisfactory corrosion resistance for a well-defined application is not impossible when the austenitic and other types of stainless steels are fusion or resistance welded; in fact, tolerable properties are more regularly obtained than might be envisaged. The main problems that might be encountered are weld decay, knifeline attack and stress-corrosion cracking (Fig. 9.29).

Weld decay is the result of the intergranular precipitation of chromium carbide in the temperature range of 450–800°C and material in this condition is referred to as being 'sensitised'. Sensitisation depletes the matrix in the grain-boundary region of chromium and this region may eventually suffer intergranular corrosion (see Section 3.3). During welding some zone in the vicinity of the weld area is inevitably raised within the sensitisation temperature range and the degree of severity of sensitisation will be dependent on a number of process factors that determine the time in this temperature range, e.g. heat input, thickness of plate. For most commercial grades of stainless steel in thin section (<10 mm) the loss in corrosion resistance is slight and seldom warrants any special measures. For a high degree of corrosion resistance, or in welded thick plate, it becomes necessary to take one of the following courses of action:

1. Thermally treat the structures to effect a re-solution of the chromium carbide; this is often impractical in large structures unless local heat treatment is employed, but is not always satisfactory since a sensitised zone could be produced just outside the local thermally treated region.
2. Use extra-low-carbon steel.
3. Use stabilised steels, i.e. austenitic steels containing niobium, tantalum or titanium.

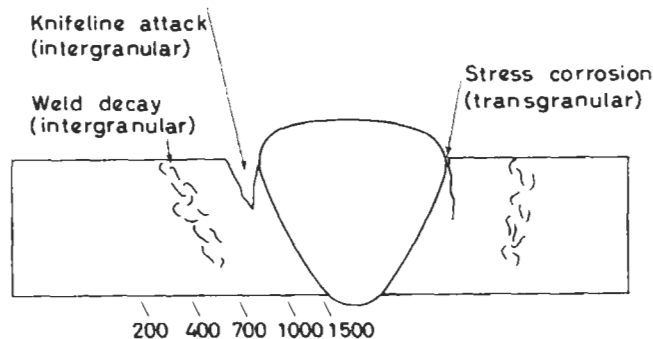


Fig. 9.29 Corrosion sites in stainless steel welds. The typical peak temperatures attained during welding (°C) are given at the foot of the diagram. Note that knifeline attack has the appearance of a sharply defined line adjacent to the fusion zone

It is important to note that the filler metals should also be stabilised, particularly in a multi-run weld where previous deposits are obviously going to be thermally cycled as later runs are deposited. It may also be necessary to increase the nickel and chromium contents of the filler to offset losses incurred during welding.

It should be noted that sensitisation has very little effect on mechanical properties and that intergranular attack occurs only in environments that are aggressive. France and Greene²² point out that the precautions taken to avoid sensitisation are frequently unnecessary, and they have carried out a potentiostatic study of a number of electrolyte solutions to evaluate the range of potential, composition and temperature in which intergranular attack occurs. They claim that by means of these studies it is possible to predict whether the environment will be aggressive or non-aggressive to the sensitised zone, and that in the case of the latter no precautions need be taken to avoid sensitisation. This work, which has been criticised by Streicher²³, is still controversial and generally the normal precautions concerning sensitisation are taken irrespective of the nature of the environment.

Titanium stabilised fillers should not be used in argon-arc welding as titanium will be vaporised and its effectiveness as a stabiliser lost. Carburising the weld seam by pick-up from surface contamination, electrode coatings or the arc atmosphere leads to increased tendency to intercrystalline corrosion.

The effect of the welding process on the severity of weld decay varies according to the process and the plate thickness so that no single recommendation is possible for every thickness of plate if resistance to attack is essential. The severity of weld decay correlates quite well with sensitisation times as calculated from recorded weld heating cycles.

Under certain conditions it is possible for a weldment to suffer corrosive attack which has the form of a fusion line crack emanating from the toe of the weld; this is termed *knifeline attack*. It is occasionally experienced in welded stabilised steels after exposure to hot strong nitric acids. The niobium-stabilised steels are more resistant than the titanium-stabilised types by virtue of the higher solution temperature of NbC, but the risk may be minimised by limiting the carbon content of a steel to 0.06% maximum (ELC steel).

Stress-corrosion cracking (Chapter 8) is particularly dangerous because of the insidious nature of the phenomenon. The residual stresses arising from welding are often sufficiently high to provide the necessary stress condition whilst a chloride-containing environment in contact with the austenitic stainless steels induces the typically transgranular and branched cracking. An increased nickel content marginally improves the resistance of the steel to this type of attack, whilst at the opposite extreme, the ferritic chromium steels are not susceptible. The only sure means of eliminating this hazard is to employ either a stress-relief anneal or a molybdenum-bearing steel, but stabilised steels must be used since the required heat treatment is in the carbide-sensitisation temperature range.

Nickel Alloys (Section 4.5)

In the main, welding does not seriously affect the corrosion resistance of the high nickel alloys and stress relief is not generally required since the resistance to stress corrosion is particularly high; this property increases with increase in nickel content and further improvement may be obtained by the addition of silicon. The chromium-containing alloys can be susceptible to weld decay and should be thermally stabilised with titanium or niobium, and where conditions demand exposure to corrosive media at high temperatures a further post-weld heat treatment may be desirable. For the Ni-Cr-Mo-Fe-W type alloys, Samans²⁴ suggests that the material should be given a two-stage heat treatment prior to single-pass welding in order to produce a dependable microstructure with a thermally stabilised precipitate.

The Ni-28Mo alloy provides a special case of selective corrosion analogous to the weld-decay type of attack; it may be removed by solution treatment or using an alloy containing 2% V²⁵.

Of the weldability problems, nickel and nickel-based alloys are particularly prone to solidification porosity, especially if nitrogen is present in the arc atmosphere, but this may be controlled by ensuring the presence of titanium as a denitrider in the filler and maintaining a short arc length. The other problem that may be encountered is hot cracking, particularly in alloys containing Cr, Si, Ti, Al, B, Zr, S, Pb and P.

For optimum corrosion resistance it is recommended that similar composition fillers be used wherever possible, and obviously any flux residues that may be present must be removed.

Aluminium Alloys (Section 4.1)

These alloys are very susceptible to hot cracking and in order to overcome this problem most alloys have to be welded with a compensating filler of different composition from that of the parent alloy, and this difference in composition may lead to galvanic corrosion. A further problem in the welding of these materials is the high solubility of the molten weld metal for gaseous hydrogen which causes extensive porosity in the seam on solidification; the only effective remedy is to maintain the hydrogen potential of the arc atmosphere at a minimum by using a hydrogen-free gas shield with dry, clean consumables (e.g. welding rods, wire) and parent plate.

In general, the corrosion resistance of many of the alloys is not reduced by welding. Any adverse effects that may be encountered with the high-strength alloys can be largely corrected by post-weld heat treatment; this is particularly true of the copper-bearing alloys. Pure aluminium fillers impart the best corrosion resistance, although the stronger Al-Mg and Al-Mg-Si fillers are normally suitable; the copper-bearing fillers are not particularly suitable for use in a corrosive environment. Resistance welding does not usually affect the corrosion resistance of the aluminium alloys.

The heat-affected zone may become susceptible to stress-corrosion cracking, particularly the high-strength alloys, and expert advice is necessary

Table 9.9 Possible problems in less commonly welded metals

<i>Metal</i>	<i>Weldability</i>	<i>Corrosion</i>
Copper alloys	Porosity	De-zincification
	Hot cracking	De-aluminification
	Hot tearing	Stress corrosion
	Steam explosion	
Magnesium alloys	Porosity	Stress corrosion
	Hot cracking	Pitting
	Lack of fusion	
Titanium alloys	Porosity	Stress corrosion
	Embrittlement	

concerning the suitability of a particular alloy for a certain environment after welding. In this context Al-Zn-Mg type alloys have been extensively studied²⁶ and it has been shown that maximum sensitivity appears to occur when there is a well-developed precipitation at the heat-affected zone grain boundaries adjacent to the fusion line, a fine precipitate within the grain and a precipitate-free zone immediately adjacent the grain boundaries. The action of stress-corrosion cracking then appears to be a result of local deformation in the precipitate-free zone combined with the anodic character of the precipitate particles.

Other Materials

Space does not permit a survey of all the various weldable metals and their associated problems, although some suggestions are made in Table 9.9. It is sufficient to state that with a knowledge of the general characteristics of the welding process and its effects on a metal (e.g. type of thermal cycle imposed, residual stress production of crevices, likely weldability problems) and of the corrosion behaviour of a material in the environment under consideration, a reliable joint for a particular problem will normally be the rule and not the exception.

Corrosion Fatigue (Section 8.6)

A metal's resistance to fatigue is markedly reduced in a corrosive environment. Many welded structures are subjected to fluctuating stresses which, with the superimposed tensile residual stress of the joint, can be dangerous. In addition to this a welded joint is a discontinuity in an engineering structure containing many possible sites of stress concentration, e.g. toe or root of the joint, weld ripple.

Protection of Welded Joints

Structural steels are frequently protected from corrosion by means of a paint primer, but these materials can have an adverse effect on the

subsequent welding behaviour and this is mainly observed as porosity¹³. Hot-dip galvanising for long-term protection can also lead to porosity and intergranular cracking after welding, in which case it may be necessary to remove the zinc coating from the faying edges prior to welding. The presence of zinc can also lead to operator problems due to the toxicity of the fume evolved unless adequate fume extraction is employed.

Prior to painting, all welding residues must be removed and the surface prepared by grinding, grit blasting, wire brushing or chemical treatment. This preparation is of fundamental importance, the method of applying the paint and the smoothness of the bead apparently having little effect on the final result²⁷.

Recent Developments

Although the problems associated with the corrosion and protection of jointed structures have been recognised since the early days of structural fabrication, they have taken on a special significance in the past 15 years. The motivation for the increased impetus is mainly one of concern over possible costly, hazardous or environmentally unfriendly failures particularly those concerned with offshore constructions, nuclear reactors, domestic water systems, food handling, waste disposal and the like.

The subject of weldment corrosion in offshore engineering has been well reviewed by Turnbull²⁹. Galvanic effects are possible if the steel weld metal is anodic to the surrounding parent plate and is enhanced by the high anode to cathode surface area ratio that exists. Lundin³⁰ showed that basic ferritic weld metal has a more electronegative potential, acid ferritic weld metal is the most electropositive, whilst rutile ferritic weld metal is intermediate between the two. The nature of the surface and its prior treatment (eg. peening) seemed to have no effect. It was also noted that the heat affected zone (HAZ) was no less corrosion resistant than the unaffected plate. Millscale, an electronically conducting oxide of Fe, should be removed by mill-blasting as its presence can cause serious galvanic effects around the joints. On the other hand, Saarinen and Onnela³¹ considered that weld metal corrosion can be eliminated by using a suitably balanced electrode type, the remaining problem then being in the HAZ whose corrodibility increased with increasing Mn content. This was related to the effect of Mn on the transformation characteristics of Fe. Thus, the heat input during welding must be important since the significant factor will be the cooling rate of the HAZ after welding. These findings have been substantiated by Ousyannikov *et al.*³² using a scanning comparative electrode probe. Increasing the heat input changed the weld metal from anodic to cathodic relative to the parent plate, although the presence of Ni reduced the magnitude of the effect.

Recently, attention has been directed to a study of the problem of grooving corrosion in line-pipe steel welded by high frequency induction or electric resistance welding. In sea water, it seems to be related to high sulphur content in the weld zone, the type of environment, its temperature and velocity^{33,34}. The importance of sulphur is significant since Drodten and Herbsleb have reported that localised corrosion at welded joints is more a

function of S, Si, microstructure, and non-metallic inclusion type and shape than of the local oxygen concentration³⁵.

One of the major concerns in offshore construction is that of corrosion fatigue. Turnbull²⁹ discusses this at length. Cracks usually originate at weld toes, the point of initiation being associated with crack-like defects (slag, non-metallics, cold laps, undercuts, hot tears). These can constitute sharp notches situated at a point of maximum stress concentration due to the weld geometry. It is to be noticed that although cracks initiate in the HAZ at the weld toe, the majority of crack propagation occurs in what is essentially unaffected parent plate. In air, it is possible to have cracks that grow at a decelerating rate until no further growth occurs; this is the 'short crack' problem widely discussed by Miller³⁶, and the cracks are referred to as non-propagating cracks. On the other hand, the same cracks may continue to grow at an accelerating rate in a corrosive environment even though the stress may be below the fatigue limit; this has been studied little until recently. Burns and Vosikovsky³⁷ have given considerable attention to corrosion fatigue of tubular joints in the BS4360:50 type steels and X65 line-pipe steels. Initiation at the toe occurs after a small fraction of life and long surface cracks can exist for over 50% of the life. On the other hand, laboratory tests on plate-to-plate welded specimens of the cruciform type show cracks which are much smaller for a larger percentage of the life but their growth rate accelerates as the depth increases.

In sea water, the effects of cyclic frequency, stress ratio, electrochemical potential, oxygen content and intermittent immersion at 5–12°C have all been evaluated³⁷. There is some evidence that at the lower temperatures, the seawater is less detrimental to fatigue life, but at all temperatures studied, crack growth rate was always faster than in air. At intermediate ranges of ΔK^* , there was a significant reduction in crack growth rate as the seawater temperature was reduced from 25°C to 0°C. Crack growth rate increased with cathodic protection as a result of absorption of H at the crack tip. Whilst the cracks are small and ΔK low, calcareous blocking is very effective and under these conditions cathodic protection (CP) reduces the crack growth rate. As the crack length increases, blocking becomes less effective and the increased hydrogen embrittlement can accelerate the growth rate to values greater than experienced for the unprotected joints. In the same vein, Nibbering *et al.*³⁸ obtained data showing that CP raises the initial fatigue crack resistance but has little effect at a later stage of crack propagation. Even so, they considered that CP is still the most effective method for prolonging structural life under corrosion fatigue conditions. This is not unreasonable since crack initiation and early growth can represent a large proportion of the total life.

Marine fouling leading to the local production of H_2S increases crack growth rate, but what the effect is when combined with CP is uncertain. Some of the factors mentioned earlier in connection with other steel corrosion problems are important to sulphide stress-corrosion cracking, (SSCC), eg. compositions, particularly C which usefully can be reduced to below 0.05%, S, microstructure and segregation³⁸⁻⁴⁰. Compositional homogenisation by heat treatment can be beneficial⁴¹, whilst the presence of Cu in the

* See Sections 8.6 and 8.9.

steel may have some merit⁴². SSCC of weld repairs in well-head alloys was investigated by Watkins and Rosenberg⁴³ who found that the repairs were susceptible to this problem because of the hard HAZs developed by welding. Post-weld heat treatment was an essential but not complete cure compared with unrepaired castings. In the case of hydrogen-assisted cracking of welded structural steels, composition is more important than mechanical properties and the carbon equivalent should be $<0.5\%$ ^{44,45}.

McMinn has presented much useful data concerning the fatigue crack growth rate in simulated HAZs of A533-B steels⁴⁶, whilst Ray *et al.* have demonstrated the role of pitting corrosion of mild steel on crack initiation⁴⁷. It should not be considered that corrosion fatigue is confined to welds in seawater; Trimmer and Jarman have done extensive work on the corrosion fatigue of Ag-based brazed stainless-steel wires in artificial saliva as part of a programme to improve the life of orthodontic devices⁴⁸.

The electrochemical examination of fusion joints between nine pairs of dissimilar metal couples in seawater showed that in most cases the HAZ was anodic to the weld metals⁴⁹. Prasad Rao and Prasanna Kumar⁵⁰ undertook electrochemical studies of austenitic stainless steel claddings to find that heat input and δ Fe content significantly affected the anodic polarisation behaviour under active corrosion conditions whilst Herbsleb and Stoffelo found that two-phased weld claddings of the 24Cr-13Ni type were susceptible to inter-granular attack (IGA) as a result of sensitisation after heat treatment at 600°C ⁵¹; I_{pass} was unaffected by heat input.

IGA, pitting and crevice corrosion are problems commonly associated with the stainless steels and their welds. Of topical interest are the duplex stainless steels whose corrosion resistance, particularly in terms of pitting and crevice corrosion, depends on microstructure, e.g. the relative proportions of α Fe and γ Fe, the presence of soluble nitrogen, and the segregation of alloying elements between the α Fe and γ Fe phases⁵²⁻⁵⁶. These may be affected by heat input and welding procedures⁵⁷. Grekula *et al.*⁵⁸, studying the pitting of 316 GTA welds, found that solidification mode, although affecting segregation intensity, has only a secondary effect on pitting resistance. The final interdendritic regions to solidify in primary γ Fe welds and the δ Fe- γ Fe interfaces in primary δ Fe welds are the most susceptible sites for pit initiation. The latter is likely to be a function of the energy associated with the δ Fe- γ Fe interfaces⁵⁹ and whether the δ Fe is formed during solidification or by a solid state transformation⁶⁰. Sulphur affects pitting potential and increases the pit density but has no effect on the pit growth rate⁵⁸. Also, pitting in or adjacent to TIG weld beads in tap-water may be caused by the surface oxides formed during welding and is generally due to inadequate root gas shielding^{61,62}.

Controlled additions of N have been made to 439 steel weld metal to prevent IGA⁶³ whilst additions of Y or Ce to an 18Cr-12Ni steel have been found to be beneficial^{64,65}. In the case of TIG-welded Mo-containing stainless steels, σ -phase formation can be responsible for IGA in hot oxidising acids^{66,67}.

Jarman and Cihâl have made a study of the related IGA problem of knifeline attack (KLA) also associated with the HAZs of welded stainless steels⁶⁸. They considered that there are two manifestations of KLA of similar appearance. One is classical IGA which they refer to as KLA, whilst

the other form is a result of constitutional liquation resulting in the formation of a NbC-Fe grain boundary eutectic soluble under hot oxidising conditions; this they call fissure attack. More recent work by one of the authors suggests that dendritic TiC at the austenite grain boundary may be more damaging than NbC⁶⁹.

The stress-corrosion cracking susceptibility of 18/8 stainless steel weld metal seems to be decreased as a result of the presence of dissolved N particularly when the problem is associated with the δ Fe/ γ Fe phase interfaces⁷⁰; this is no doubt a result of the role of nitrogen as an austenite stabiliser (incidentally, it also improves the pitting resistance)⁷¹. Klueh and King identified stress-corrosion cracking failure of a joint between austenitic stainless steel and a 2.25Cr-Mo heat-resisting steel adjacent to the fusion line, and found that it was caused by the presence of metallurgical structural changes present⁷².

Stress-corrosion cracking of welded Al-Zn-Mg alloys is still a popular research area^{73,74}. Scanning electron microscopy has confirmed that the enhanced susceptibility to stress-corrosion cracking due to an applied anodic over-voltage is not caused by anodic dissolution at the crack tip but by hydrogen embrittlement. The most resistant alloys have a Zn:Mg ratio of 3 and Zn + Mg > 7%. The role of H appears to be logical from the work of Patel and Jarman who have reported the magnitude of the strain field around the tip of propagating cracks in Al-Zn-Mg⁷⁵. This field is under constant review by Holroyd and Hardie⁷⁶.

General corrosion damage was the cause of failure of an Al alloy welded pipe assembly in an aircraft bowser which was attacked by a deicing-fluid-water mixture at small weld defects⁷⁷. Selective attack has been reported in welded cupro-nickel subjected to estuarine and seawater environments⁷⁸. It was the consequence of the combination of alloy element segregation in the weld metal and the action of sulphate reducing bacteria (SRB). Sulphide-coated Cu-enriched areas were cathodic relative to the adjacent Ni-rich areas where, in the latter, the sulphides were being continuously removed by the turbulence. Sulphite ions seemed to act as a mild inhibitor.

General corrosion occurs in the weld metal and HAZ of welded Zr-2.25Nb alloys in an environment of H₂SO₄ at temperatures greater than 343 K, the rate increasing with concentration. Above 70% H₂SO₄ both general corrosion and IGA occur, whilst above 80% hydrogen embrittlement was found also. Sulphides were found to be deposited on the metal surface^{79,80}.

Protection of welds, both before and after welding, is worthy of careful consideration. For example, in the electric-resistance welding of hot-dipped galvanised steel, welding had little effect on the seawater corrosion of the coated steel when compared with the uncoated steel, the latter showing considerable corrosion after 12 months exposure⁸¹. The subject of galvanising and the welding of structural steels has been given special attention by Porter⁸², but by far the most common method of protection is by painting which McKelvie⁸³ discusses in terms of fundamentals of paint as a corrosion barrier and the cleaning and coating procedures necessary to achieve protection of welded structures. In these articles he covers the type of contaminants arising from welding as well as cleaning methods, blast primers, galvanising, coating removal for repair welding, wire brushing and chemical

treatments. Lloyds Register of Shipping lists the proprietary products that have no significant deleterious effects on subsequent welding work⁸⁴.

Soldered joints present their own characteristic corrosion problems usually in the form of dissimilar metal attack often aided by inadequate flux removal after soldering. Such joints have always been a source of concern to the electrical industry^{85,86}. Lead-containing solders must be used with caution for some types of electrical connection since $\text{Pb}(\text{OH})_2 \cdot \text{PbCO}_3$ may be found as a corrosion product and can interrupt current flow. Indium has been found to be a useful addition to Sn-Pb solders to improve their corrosion resistance⁸⁷. However, in view of the toxicity of lead and its alloys, the use of lead solders, particularly in contact with potable waters and food-stuffs, is likely to decline.

In the related process of brazing, crevice corrosion has been found when joining copper tubes using Cu-Ag-P fillers, the presence of scale adjacent to the joint being deemed responsible⁸⁸. Interface corrosion of brazed stainless steel joints has been comprehensively reviewed by Kuhn and Trimmer⁸⁹ whilst Lewis⁹⁰ has used photo-electron spectroscopy to confirm the dezincification theory. As a technical problem it has been reported as occurring in contact with the drink sake with the further complication that the eluted Fe^{3+} ions from the corrosion of the stainless steel gave rise to discoloration of the liquid⁹¹. On the other hand, the corrosion resistance of a high temperature brazed joint in a Mo-containing low-C stainless steel exposed to drinking water gave no problems⁹². Sukanuma *et al.* reported an unusual instance of the stress-corrosion cracking of SiN brazed with Al when subjected to an environment of water⁹³. It was contended that the interfacial region was weakened as a result of the surface layers of the SiN being deformed by the grinding operation used prior to brazing. A pre-heat treatment of the SiN at a temperature of no less than 1 100 K was found to remove the damage.

Finally, mechanical joints, e.g. nuts, bolts, rivets etc., are still important joining methods for which attention must be given to compatibility to avoid dissimilar metal corrosion problems and crevice corrosion⁹⁴⁻⁹⁸.

Conclusions

Every type of corrosion and oxidation problem can be encountered in jointed structures and it is obvious that most engineering structures must be jointed. It would appear therefore, that all structures are on the verge of disintegration. Yet, for every jointed structure that fails by corrosion, there are many hundreds of thousands which have survived the test of time. With a reasonable knowledge of the mechanics of jointing, the possible design and process factors (e.g. crevices, dissimilar materials in contact, presence of fluxes), a basic understanding of corrosion science and, above all, commonsense, few problems in the established fabrication fields should be encountered. As aptly pointed out by Scully²⁸, as with all other scientific and technological problems, experience is often the final arbiter.

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9.5A Appendix – Terms Commonly Used in Joining*

Automatic Welding: welding in which the welding variables and the means of making the weld are controlled by machine.

Bead: a single run of weld metal on a surface.

Braze Welding: the joining of metals using a technique similar to fusion welding and a filler metal with a lower melting point than the parent metal, but neither using capillary action as in brazing nor intentionally melting the parent metal.

Brazing: a process of joining metals in which, during or after heating, molten filler metal is drawn by capillary action into the space between closely adjacent surfaces of the parts to be joined. In general, the melting point of the filler metal is above 500°C, but always below the melting temperature of the parent metal.

Brazing Alloy: filler metal used in brazing.

Butt Joint: a connection between the ends or edges of two parts making an angle to one another of 135° to 180° inclusive in the region of the joint.

Carbon Dioxide Welding: metal-arc welding in which a bare wire electrode is used, the arc and molten pool being shielded with carbon dioxide gas.

Covered Filler Rod: a filler rod having a covering of flux.

Deposited Metal: filler metal after it becomes part of a weld or joint.

Edge Preparation: squaring, grooving, chamfering or bevelling an edge in preparation for welding.

Electro-slag Welding: fusion welding utilising the combined effects of current and electrical resistance in a consumable electrode and conducting bath of molten slag, through which the electrode passes into a molten pool, both the pool and the slag being retained in the joint by cooled shoes which move progressively upwards.

Electron-beam Welding: fusion welding in which the joint is made by fusing the parent metal by the impact of a focused beam of electrons.

* Data extracted from BS 499: Part 1 (1965). Complete copies of this standard can be obtained from The British Standards Institution, Information Department, Linford Wood, Milton Keynes, MK 14 6 LE.

Filler Metal: metal added during welding, braze welding, brazing or surfacing.

Filler Rod: filler metal in the form of a rod. It may also take the form of filler wire.

Flux: material used during welding, brazing or braze welding to clean the surfaces of the joint, prevent atmospheric oxidation and to reduce impurities.

Fusion Penetration: depth to which the parent metal has been fused.

Fusion Welding: welding in which the weld is made between metals in a molten state without the application of pressure.

Fusion Zone: the part of the parent metal which is melted into the weld metal.

Heat-affected Zone: that part of the parent metal which is metallurgically affected by the heat of the joining process, but not melted.

Hydrogen Controlled Electrode: a covered electrode which, when used correctly, produces less than a specified amount of diffusible hydrogen in the weld deposit.

Manual Welding: welding in which the means of making the weld are held in the hand.

Metal-arc Welding: arc welding using a consumable electrode.

MIG-welding: metal-inert gas arc welding using a consumable electrode.

Oxyacetylene Welding: gas welding in which the fuel gas is acetylene and which is burnt in an oxygen atmosphere.

Parent Metal: metal to be joined.

Pressure Welding: a welding process in which a weld is made by a sufficient pressure to cause plastic flow of the surfaces, which may or may not be heated.

Resistance Welding: welding in which force is applied to surfaces in contact and in which the heat for welding is produced by the passage of electric current through the electrical resistance at, and adjacent to, these surfaces.

Run: the metal melted or deposited during one passage of an electrode, torch or blow-pipe.

Semi-automatic Welding: welding in which some of the variables are automatically controlled, but manual guidance is necessary.

Spatter: globules of metal expelled during welding onto the surface of parent metal or of a weld.

Spelter: a brazing alloy consisting nominally of 50% Cu and 50% Zn.

Submerged-arc Welding: metal-arc welding in which a bare wire electrode is used; the arc is enveloped in flux, some of which fuses to form a removable covering of slag on the weld.

TIG-welding: tungsten inert-gas arc welding using a non-consumable electrode of pure or activated tungsten.

Thermal Cutting: the parting or shaping of materials by the application of heat with or without a stream of cutting oxygen.

Weld: a union between pieces of metal at faces rendered plastic or liquid by heat or by pressure, or by both. A filler metal whose melting temperature is of the same order as that of the parent material may or may not be used.

Welding: the making of a weld.

Weld Metal: all metal melted during the making of a weld and retained in the weld.

Weld Zone: the zone containing the weld metal and the heat-affected zone.

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10 CATHODIC AND ANODIC PROTECTION

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10.1 Principles of Cathodic Protection

Cathodic protection is unique amongst all the methods of corrosion control in that if required it is able to stop corrosion completely, but it remains within the choice of the operator to accept a lesser, but quantifiable, level of protection. Manifestly, it is an important and versatile technique.

In principle, cathodic protection can be applied to all the so-called engineering metals. In practice, it is most commonly used to protect ferrous materials and predominantly carbon steel. It is possible to apply cathodic protection in most aqueous corrosive environments, although its use is largely restricted to natural near-neutral environments (soils, sands and waters, each with air access). Thus, although the general principles outlined here apply to virtually all metals in aqueous environments, it is appropriate that the emphasis, and the illustrations, relate to steel in aerated natural environments.

The text seeks to show why it is that cathodic protection is apparently so restricted in its scope of application despite its apparent versatility. Nevertheless, having recognised the restricted scope it is important to emphasise that the number and criticality of the structures to which cathodic protection is applied is very high indeed.

Historical

In recent years it has been regarded as somewhat passé to refer to Sir Humphrey Davy in a text on cathodic protection. However, his role in the application of cathodic protection should not be ignored. In 1824 Davy presented a series of papers to the Royal Society in London¹ in which he described how zinc and iron anodes could be used to prevent the corrosion of copper sheathing on the wooden hulls of British naval vessels. His paper shows a considerable intuitive awareness of what are now accepted as the principles of cathodic protection. Several practical tests were made on vessels in harbour and on sea-going ships, including the effect of various current densities on the level of protection of the copper. Davy also considered the use of an impressed current device based on a battery, but did not consider the method to be practicable.

The first 'full-hull' installation on a vessel in service was applied to the frigate HMS *Samarang* in 1824. Four groups of cast iron anodes were fitted and virtually perfect protection of the copper was achieved. So effective was the system that the prevention of corrosion of the copper resulted in the loss of the copper ions required to act as a toxicide for marine growth leading to increased marine fouling of the hull. Since this led to some loss of performance from the vessel, interest in cathodic protection waned. The beneficial action of the copper ions in preventing fouling was judged to be more important than preventing deterioration of the sheathing. Cathodic protection was therefore neglected for 100 years after which it began to be used successfully by oil companies in the United States to protect underground pipelines².

It is interesting that the first large-scale application of cathodic protection by Davy was directed at protecting copper rather than steel. It is also a measure of Davy's grasp of the topic that he was able to consider the use of two techniques of cathodic protection, viz. sacrificial anodes and impressed current, and two types of sacrificial anode, viz. zinc and cast iron.

Electrochemical Principles

Aqueous Corrosion

The aqueous corrosion of iron under conditions of air access can be written:



The product, ferrous hydroxide, is commonly further oxidised to magnetite (Fe_3O_4) or a hydrated ferric oxide (FeOOH), i.e. rust.

It is convenient to consider separately the metallic and non-metallic reactions in equation 10.1:



To balance equations 10.2 and 10.3 in terms of electrical charge it has been necessary to add four electrons to the right-hand side of equation 10.2 and to the left-hand-side of equation 10.3. However, simple addition and rationalisation of equations 10.2 and 10.3 yields equation 10.1.

We conclude that corrosion is a chemical reaction (equation 10.1) occurring by an electrochemical mechanism (equations 10.2) and (10.3), i.e. by a process involving electrical and chemical species. Figure 10.1 is a schematic representation of aqueous corrosion occurring at a metal surface.

Equation 10.2, which involves consumption of the metal and release of electrons, is termed an *anodic* reaction. Equation 10.3, which represents consumption of electrons and dissolved species in the environment, is termed a *cathodic* reaction. Whenever spontaneous corrosion reactions occur, all the electrons released in the anodic reaction are consumed in the cathodic reaction; no excess or deficiency is found. Moreover, the metal normally takes up a more or less uniform electrode potential, often called the corrosion or mixed potential (E_{corr}).

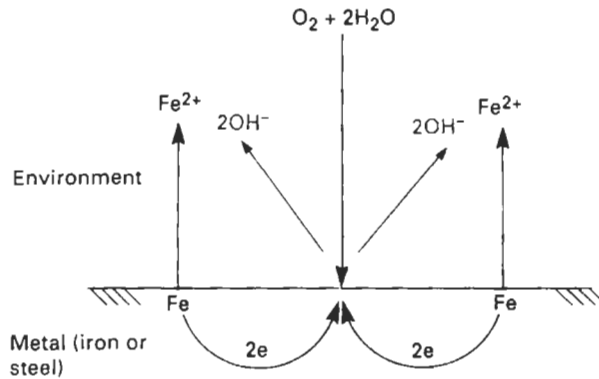


Fig. 10.1 Schematic illustration of the corrosion of steel in an aerated environment. Note that the electrons released in the anodic reaction are consumed quantitatively in the cathodic reaction, and that the anodic and cathodic products may react to produce $\text{Fe}(\text{OH})_2$

Cathodic Protection

It is possible to envisage what might happen if an electrical intervention was made in the corrosion reaction by considering the impact on the anodic and cathodic reactions. For example, if electrons were withdrawn from the metal surface it might be anticipated that reaction 10.2 would speed up (to replace the lost electrons) and reaction 10.3 would slow down, because of the existing shortfall of electrons. It follows that the rate of metal consumption would increase.

By contrast, if additional electrons were introduced at the metal surface, the cathodic reaction would speed up (to consume the electrons) and the anodic reaction would be inhibited; metal dissolution would be slowed down. This is the basis of cathodic protection.

Figure 10.2 shows the effect on the corrosion reaction shown in Fig. 10.1 of providing a limited supply of electrons to the surface. The rate of dissolution slows down because the external source rather than an iron atom provides two of the electrons. Figure 10.3 shows the effect of a greater electron supply; corrosion ceases since the external source provides all the requisite electrons. It should be apparent that there is no reason why further electrons could not be supplied, when even more hydroxyl (OH^-) ion would be produced, but without the possibility of a concomitant reduction in the rate of iron dissolution. Clearly this would be a wasteful exercise.

The corrosion reaction may also be represented on a polarisation diagram (Fig. 10.4). The diagram shows how the rates of the anodic and cathodic reactions (both expressed in terms of current flow, I) vary with electrode potential, E . Thus at E_a , the net rate of the anodic reaction is zero and it increases as the potential becomes more positive. At E_c the net rate of the cathodic reaction is zero and it increases as the potential becomes more negative. (To be able to represent the anodic and cathodic reaction rates on the same axis, the modulus of the current has been drawn.) The two reaction rates are electrically equivalent at E_{corr} , the corrosion potential, and the

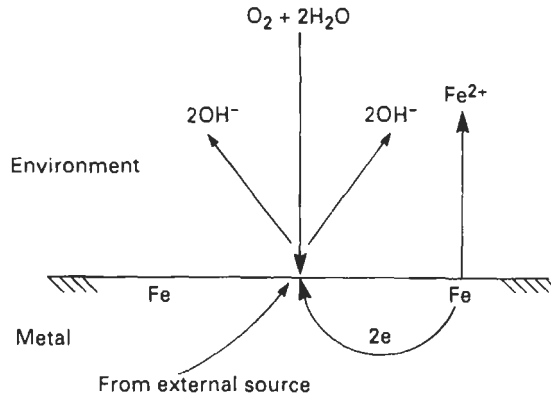


Fig. 10.2 Schematic illustration of partial cathodic protection of steel in an aerated environment. Note that one of the anodic reactions shown in Fig. 10.1 has been annihilated by providing two electrons from an external source; an excess of OH^- ions over Fe^{2+} now exists at the surface

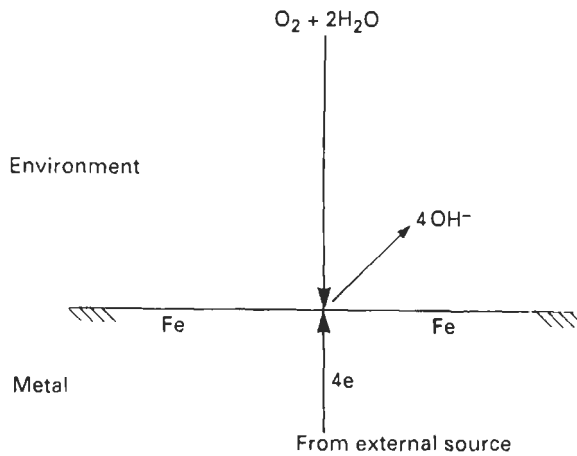


Fig. 10.3 Schematic illustration of full cathodic protection of steel in an aerated environment. Note that both anodic reactions shown in Fig. 10.1 have now been annihilated and there is an accumulation of OH^- at the surface

corresponding current, I_{corr} is an electrical representation of the rate of the anodic and cathodic reactions at that potential, i.e. the spontaneous corrosion rate of the metal. That is, at E_{corr} the polarisation diagram represents the situation referred to above. Namely, that when spontaneous corrosion occurs, the rate of electron release equals the rate of electron consumption, and there is no net current flow although metal is consumed, and meanwhile the metal exerts a single electrode potential.

To hold the metal at any potential other than E_{corr} requires that electrons be supplied to, or be withdrawn from, the metal surface. For example, at E' the cathodic reaction rate, I'_c , exceeds the anodic reaction rate, I'_a , and the latter does not provide sufficient electrons to satisfy the former. If the

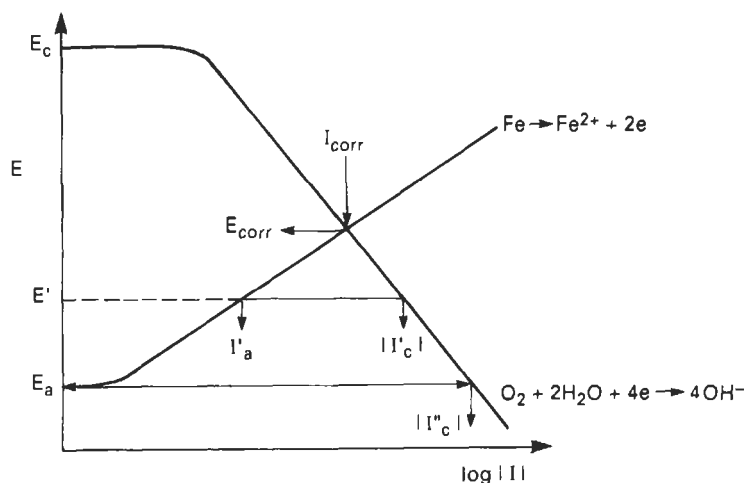


Fig. 10.4 Polarisation diagram representing corrosion and cathodic protection. A corroding metal takes up the potential E_{corr} spontaneously and corrodes at a rate given by I_{corr} . If the potential is to be lowered to E' a current equal to $(|I'_c| - I'_a)$ must be supplied from an external source; the metal will then dissolve at a rate equal to I'_a .

metal is to be maintained at E' , the shortfall of electrons given by $(|I'_c| - I'_a)$ must be supplied from an external source. This externally supplied current serves to reduce the metal dissolution rate from I_{corr} to I'_a .

At E_a the net anodic reaction rate is zero (there is no metal dissolution) and a cathodic current equal to I''_c must be available from the external source to maintain the metal at this potential. It may also be apparent from Fig. 10.4 that, if the potential is maintained below E_a , the metal dissolution rate remains zero ($I_a = 0$), but a cathodic current greater than I''_c must be supplied; more current is supplied without achieving a benefit in terms of metal loss. There will, however, be a higher interfacial hydroxyl ion concentration.

Oxygen Reduction

In illustrating the corrosion reaction in equation 10.1, the oxygen reduction reaction (equation 10.3) has been taken as the cathodic process. Moreover, in Figs 10.1 to 10.4 oxygen reduction has been assumed. Whilst there is a range of cathodic reactions that can provoke the corrosion of a metal (since to be a cathodic reactant any particular species must simply act as an oxidising agent to the metal) the most common cathodic reactant present in natural environments is oxygen. It is for this reason that the oxygen reduction reaction has been emphasised here.

When corrosion occurs, if the cathodic reactant is in plentiful supply, it can be shown both theoretically and practically that the cathodic kinetics are semi-logarithmic, as shown in Fig. 10.4. The rate of the cathodic reaction is governed by the rate at which electrical charge can be transferred at the metal surface. Such a process responds to changes in electrode potential giving rise to the semi-logarithmic behaviour.

Because oxygen is not very soluble in aqueous solutions (ca. 10 ppm in cool seawater, for example) it is not freely available at the metal surface. As a result it is often easier to transfer electrical charge at the surface than for oxygen to reach the surface to take part in the charge transfer reaction. The cathodic reaction rate is then controlled by the rate of arrival of oxygen at the surface. This is often referred to as mass transfer control. Since oxygen is an uncharged species, its rate of arrival is unaffected by the prevailing electrical field and responds only to the local oxygen concentration gradient. If the cathodic reaction is driven so fast that the interfacial oxygen concentration is reduced to zero (i.e. the oxygen is consumed as soon as it reaches the surface), the oxygen concentration gradient to the surface reaches a maximum and the reaction rate attains a limiting value. Only an increase in oxygen concentration or an increase in flow velocity will permit an increase in the limiting value. The cathodic kinetics under mass transfer control will be as shown in Fig. 10.5.

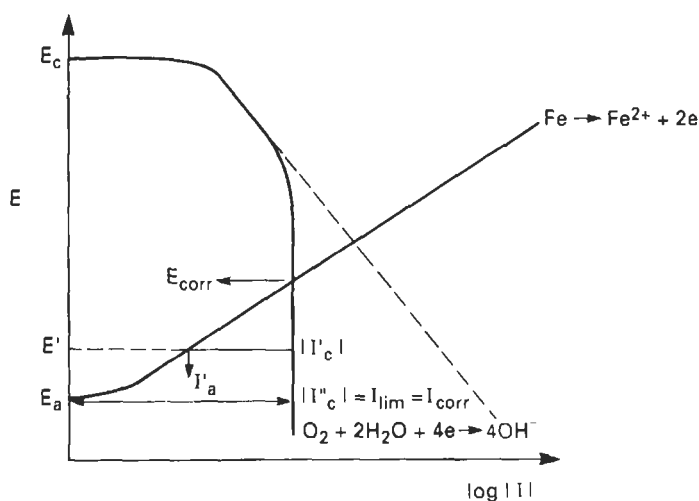


Fig. 10.5 Polarisation diagram representing corrosion and cathodic protection when the cathodic process is under mass transfer control. The values of E_{corr} and I_{corr} are lower than when there is no mass transfer restriction, i.e. when the cathodic kinetics follow the dotted line

Figure 10.5 demonstrates that, even when semi-logarithmic cathodic kinetics are not observed, partial or total cathodic protection is possible. Indeed, Fig. 10.5 shows that the corrosion rate approximates to the limiting current for oxygen reduction (I_{lim}) and the current required for protection is substantially lower than when semi-logarithmic cathodic behaviour prevails.

Hydrogen Evolution

In principle it is possible for water to act as a cathodic reactant with the formation of molecular hydrogen:



Indeed, in neutral solutions the corrosion of iron with concomitant hydrogen evolution deriving from the reduction of water is thermodynamically feasible. In practice, this cathodic reaction is barely significant because the reduction of any oxygen present is both thermodynamically favoured and kinetically easier. In the absence of oxygen, the hydrogen evolution reaction at the corrosion potential of iron is so sluggish that the corrosion rate of the iron is vanishingly small.

Nevertheless, hydrogen evolution is important in considering the cathodic protection of steel. Although hydrogen evolution takes little part in the corrosion of steel in aerated neutral solutions (see Fig. 10.6), as the potential is lowered to achieve cathodic protection so it plays a larger, and eventually dominant, role in determining the total current demand. This too is demonstrated in Fig. 10.6 where, it must be remembered, the current supplied from the external source at any potential must be sufficient to sustain the total cathodic reaction, i.e. both oxygen reduction and hydrogen evolution reactions at that potential. It will be seen that to lower the potential much below E_a entails a substantial increase in current and significantly more hydrogen evolution.

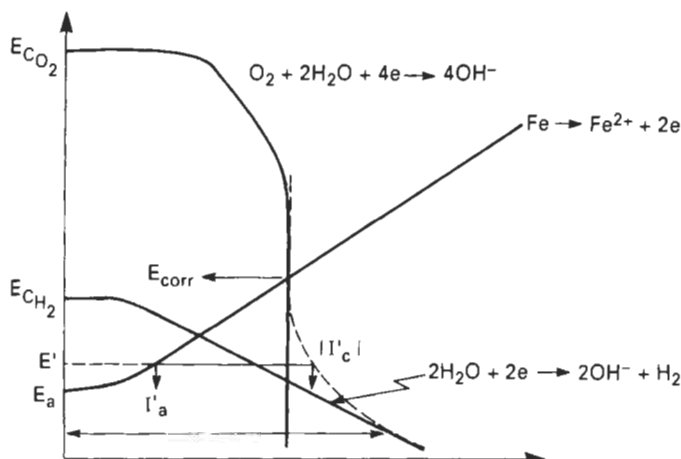


Fig. 10.6 Polarisation diagram showing the limited role hydrogen evolution plays at the corrosion potential of steel in aerated neutral solution, the larger role in determining cathodic protection currents and the dominant role in contributing to current requirements at very negative potentials. The dotted line shows the total cathodic current due to oxygen reduction and hydrogen evolution

Methods of Applying Cathodic Protection

There are two principal methods of applying cathodic protection, viz. the impressed current technique and the use of sacrificial anodes. The former includes the structure as part of a driven electrochemical cell and the latter includes the structure as part of a spontaneous galvanic cell.

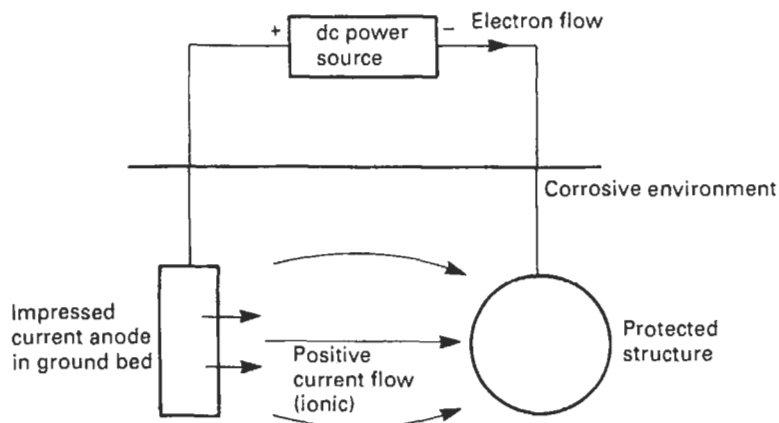


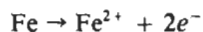
Fig. 10.7 Schematic diagram of cathodic protection using the impressed-current technique

Impressed Current Method

Figure 10.7 illustrates the use of an external power supply to provide the cathodic polarisation of the structure. The circuit comprises the power source, an auxiliary or impressed current electrode, the corrosive solution, and the structure to be protected. The power source drives positive current from the impressed current electrode through the corrosive solution and onto the structure. The structure is thereby cathodically polarised (its potential is lowered) and the positive current returns through the circuit to the power supply. Thus to achieve cathodic protection the impressed current electrode and the structure must be in both electrolytic and electronic contact.

The power supply is usually a transformer/rectifier that converts a.c. power to d.c. Typically the d.c. output will be in the range 15–100 V and 5–100 A although 200 V/200 A units are not unknown. Thus fairly substantial driving voltages and currents are available. Where mains power is not available, diesel or gas engines, solar panels or thermoelectric generators have all been used to provide suitable d.c.

It will be seen that the impressed current electrode discharges positive current, i.e. it acts as an anode in the cell. There are three generic types of anode used in cathodic protection, viz, consumable, non-consumable and semi-consumable. The consumable electrodes undergo an anodic reaction that involves their consumption. Thus an anode made of scrap iron produces positive current by the reaction:

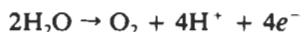


the ferrous iron entering the environment as a positive current carrier*. Since the dissolving anode must obey Faraday's law it follows that the wasting of the anode will be proportional to the total current delivered.

* In practice the cathodic protection current will be carried in the corrosive environment by more mobile ions, e.g. OH^{-} , Na^{+} , etc.

In practice the loss for an iron anode is approximately 9 kg/Ay. Thus consumable anodes must be replaced at intervals or be of sufficient size to remain as a current source for the design life of the protected structure. This poses some problems in design because, as the anode dissolves, the resistance it presents to the circuit increases. More important, it is difficult to ensure continuous electrical connection to the dissolving anode.

Non-consumable anodes sustain an anodic reaction that decomposes the aqueous environment rather than dissolves the anode metal. In aqueous solutions the reaction may be:



or in the presence of chloride ions:



Anodes made from platinised titanium or niobium fall in this category.

Because these anodes are not consumed faradaically, they should not, in principle, require replacement during the life of the structure. However, to remain intact they must be chemically resistant to their anodic products (acid and chlorine) and, where the products are gaseous, conditions must be produced which allow the gas to escape and not interfere with anode operation. This is particularly true of the platinised electrodes because they can operate at high current density ($>100 \text{ A/m}^2$) without detriment, but will then produce high levels of acidity ($\text{pH} < 2$) and large volumes of gas. Groundbed design (the way in which the anode is installed) is therefore crucial.

Although the anodes are described as non-consumable, they do suffer some loss of the thin (ca. $2.5\text{--}10 \mu\text{m}$) platinised coating. This loss, which unfortunately has become known as the wear rate although there is no question of the loss being due to mechanical wear, is usually small, related to the total current passed, and increased if the applied current has an a.c. component. Typically values for the loss rate are 8 mg/Ay for platinised titanium, which may be increased ten-fold if an a.c. component $< 100 \text{ Hz}$ is present. Negative-going current spikes, such as may be induced by a poorly designed thyristor switching device, even given otherwise clean d.c., can produce a hundred-fold increase in the rate of loss.

The semi-consumable electrodes, as the name implies, suffer rather less dissolution than Faraday's law would predict and substantially more than the non-consumable electrodes. This is because the anodic reaction is shared between oxidising the anode material (causing consumption) and oxidising the environment (with no concomitant loss of metal). Electrodes made from silicon-iron, chromium-silicon-iron and graphite fall into this category.

Table 10.1 gives a brief summary of the behaviour of some impressed current anodes and protection by impressed current is discussed in more detail in Section 10.3.

Sacrificial Anodes

Using the impressed-current technique the driving voltage for the protective current comes from a d.c. power source. The sacrificial anode technique

Table 10.1 Impressed current anode materials

<i>Material</i>	<i>Consumption rate or operating current density</i>	<i>Notes</i>
Consumable:		
Scrap iron	ca 9 kg/Ay	Cheap; suitable for buried or immersed use
Cast iron	<9 kg/Ay	Cheap; buried or immersed use; carbon skeleton reduces consumption
Semi-consumable:		
Silicon cast iron (Fe-14Si-(3 Mo))	5-50 A/m ² (in fresh water or soil)	Buried or immersed use; consumption (<1 kg/Ay); Mo reduces consumption in seawater
Graphite	2.5-10 A/m ²	Consumption rate very much less than steel or cast iron (<1 kg/Ay); chloride ions reduce consumption
Non-consumable:		
Lead alloys:		
1. Pb-6Sb-1Ag	<50-200 A/m ² (in seawater)	PbO ₂ film restrains consumption
2. Pt-activated	<50-500 A/m ² (in seawater)	PbO ₂ film protective
Platinised Ti, Ta or Nb	<1000 Am/m ² (consumption)	Discontinuities in Pt coat protected by oxide film on substrate; sensitive (<100Hz) a.c. ripple in d.c. or negative current spikes causing electrode consumption; maximum operating potential with Ti substrate: 9 V

uses the natural potential difference that exists between the structure and a second metal in the same environment to provide the driving voltage. No power source is employed. Moreover, the dissolution of the second metal, the sacrificial anode, provides the source of electrons for cathodic polarisation of the structure. Thus, whilst the impressed-current anode may be more noble or more base than the protected structure because the power source forces it to act as an anode, the sacrificial anode must be spontaneously anodic to the structure, i.e. be more negative in the galvanic series for the given environment. Thus, in principle, zinc, aluminium or magnesium could be used to protect steel, and iron used to protect copper. Figure 10.8 illustrates the use of a sacrificial anode for cathodic protection.

In practice pure metals are never used as sacrificial anodes. There are a variety of reasons for this which include the need for:

1. a reliable, reproducible and negative operating potential for the anode;
2. a high and reproducible capacity (Ah/kg) for the anode;
3. uniform dissolution of the anode so that all metal is consumed usefully in providing cathodic protection and not wastefully by mechanical loss;
4. freedom from any loss of activity by the anode due to passivation.

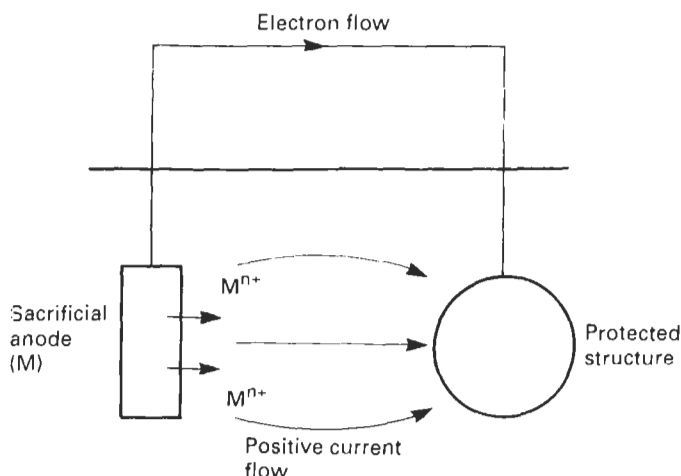


Fig. 10.8 Schematic diagram of cathodic protection using sacrificial anodes. In practice the anode, which will be mounted on a steel core, can be attached directly to the structure

For these reasons alloying elements appear in all the commercial anodes, and very careful quality control is required to keep disadvantageous tramp elements (notably iron and copper) below defined threshold levels. Many anode failures can be attributed to poor production quality control. A guide to minimum quality standards has been produced³.

Table 10.2 gives electrochemical properties for various generic anode types. It will be apparent that the driving voltages that are available from sacrificial anodes are substantially less than those available from power sources. At best an anode will produce 1 V to steel whereas an impressed current power source may produce up to 100 V.

A more detailed treatment of cathodic protection by sacrificial anodes is given in Section 10.2.

Table 10.2 Typical sacrificial anode compositions and operating parameters

<i>Alloy</i>	<i>Environment</i>	<i>Operating voltage vs. Ag/AgCl/ seawater (V)</i>	<i>Driving voltage^a (V)</i>	<i>Capacity (Ah/kg)</i>
Al-Zn-Hg	Seawater	-1.0 to -1.05	0.20 to 0.25	2600-2850
Al-Zn-In	Seawater	-1.0 to -1.10	0.20 to 0.30	2300-2650
Al-Zn-In	Marine sediments	-0.95 to -1.05	0.15 to 0.25	1300-2300
Al-Zn-Sn	Seawater	-1.0 to -1.05	0.20 to 0.25	925-2600
Zn ^b	Seawater	-0.95 to -1.03	0.15 to 0.23	760- 780
Zn ^b	Marine sediments	-0.95 to -1.03	0.15 to 0.23	750- 780
Mg-Al-Zn	Seawater	-1.5	0.7	1230
Mg-Mn	Seawater	-1.7	0.9	1230

^a The driving voltage to bare steel, i.e. protection potential of steel - anode operating potential.

^b US Military Specification.

Note: It is often important to control impurities and especially Fe, Cu, Ni and Si, although a controlled Si content is essential to some aluminium alloys.

Proof of Protection

Steel

Figure 10.4 demonstrates that the rate of dissolution of iron (or any other metal) decreases as the potential is made more negative. Figure 10.6 shows that the current required to reach any given potential below the corrosion potential (E_{corr}) will vary according to the composition of the corrosive solution. Thus Fig. 10.6 shows that, in the absence of oxygen, the current requirement would be low, but would increase to a value approximating to the limiting current in its presence. Moreover, since the limiting current can be increased by increasing the oxygen concentration or the solution flow rate, the current required for protection will change predictably with change in either of these parameters⁴. It follows that the current required to prevent corrosion completely (i.e. in principle to achieve E_a) will vary according to the environment and the environmental dynamics. As a consequence, there is no single current that will assure protection in all cases. Current supplied is not, therefore, an unequivocal indication of the effectiveness of protection.

By contrast, it appears from Figs. 10.4 and 10.6 that a potential measurement would be more reliable. Specifically that E_a (the equilibrium potential for the iron/ferrous-ion electrode given a suitably low ferrous ion concentration) would always represent the achievement of full protection for iron.

Almost without exception all the accepted criteria for full cathodic protection of iron are based on a potential measurement. The various recommended practices published by the US National Association of Corrosion Engineers (NACE) give six criteria for full protection⁵⁻¹¹. The current British Standard Code of Practice¹² gives one. These are summarised in Table 10.3. Only the first three are useful; the remainder are of dubious value or expressions of pious hope.

Table 10.3 Cathodic protection criteria^a

- | | |
|----|--|
| 1. | ≤ -0.85 V w.r.t Cu/CuSO ₄ with current applied but minimising IR error. |
| 2. | Negative shift ≥ 300 mV when current applied. |
| 3. | Positive shift ≥ 100 mV when current interrupted. |
| 4. | More negative than beginning of Tafel segment of cathodic polarisation ($E - \log I$) curve. |
| 5. | A net protective current in the structure at former anodic points. |
| 6. | Polarise all cathodic areas to open circuit potential of most active anode areas. |

^aAfter British Standard Code of Practice¹² and NACE Recommended Practices⁵⁻¹¹

The most widely accepted criterion for protection of steel at room temperature (the protection potential) in aerobic conditions is -0.85 V with respect to a Cu/CuSO₄ reference electrode. In anaerobic conditions -0.95 V (vs. Cu/CuSO₄) is the preferred protection potential because of the possible presence of active sulphate-reducing bacteria (SRB).

Various limitations on the most negative potential that may be imposed during cathodic protection are often quoted for high-strength steels (typically -1.0 V vs. Cu/CuSO₄ for steels in the 700–800 MPa tensile strength range). The restriction is to limit the evolution of hydrogen at the structure

and thereby prevent hydrogen absorption with the possibility of embrittlement of the steel possibly leading to fracture. The consequence is that the useful window of potential in which the steel can operate is severely restricted, especially under anaerobic conditions.

It must not be assumed that the protection potential is numerically equal to the equilibrium potential for the iron/ferrous-ion electrode (E_a). The standard equilibrium potential (E°) for iron/ferrous-ion is -0.440 V (vs. the standard hydrogen electrode). If the interfacial ferrous ion concentration when corrosion ceases is approximately 10^{-6} g ions/l then, according to the Nernst equation, the equilibrium potential (E_a) is given by:

$$E_a = E^\circ + \frac{0.059}{2} \log a_{\text{Fe}^{2+}}$$

where $a_{\text{Fe}^{2+}}$ is the activity or thermodynamic concentration of the ferrous cation. Thus $E_a = -0.62$ V vs. the standard hydrogen electrode or -0.93 V vs. Cu/CuSO₄. This is a value substantially more negative than the accepted protection potential (-0.85 V).

A simple calculation based on the solubility product of ferrous hydroxide and assuming an interfacial pH of 9 (due to the alkalisation of the cathodic surface by reaction³) shows that, according to the Nernst equation, at -0.85 V (vs. Cu/CuSO₄) the ferrous ion concentration then present is sufficient to permit deposition hydroxide ion. It appears that the ferrous hydroxide formed may be protective and that the practical protection potential (-0.85 V), as opposed to the theoretical protection potential ($E_a = -0.93$ V), is governed by the thermodynamics of precipitation and not those of dissolution.

It is also worth noting that the exact achievement of the so-called protection potential is not essential to excellent corrosion control. Figures 10.4 to 10.6 show the anodic kinetics as semi-logarithmic in character. Behaviour approaching this is observed in practice for steel in many environments. Thus the first increment of negative potential shift will reduce the anodic dissolution rate substantially. A second equal shift will be ten times less effective and will require the application of very much more current. A third equal shift will be ten times less effective again. That is, the dissolution rate decreases asymptotically as the full protection potential is approached; *a small shortfall in cathodic polarisation is not, therefore, disastrous*. By contrast, the current required to achieve the protection potential, and more particularly to exceed it, is often very substantial and may increase exponentially. There may often be good economic reasons for permitting a minor shortfall of polarisation.

Other Metals

In principle, all metals may be protected by cathodic protection. In practice, it is not always relevant either because the metals are, to all intents and purposes, naturally immune to corrosion (the noble metals) and often not used as engineering materials or, being base metals, they are well protected by

the spontaneous formation of a passive film in aqueous solution (aluminium or a stainless steel for example).

Copper-base alloys will corrode in aerated conditions. It is, therefore, sometimes appropriate to consider cathodic protection. It becomes particularly relevant when the flow rates are high or when the design of an item causes the copper to be an anode in a galvanic cell (e.g. a copper alloy tube plate in a titanium-tubed heat exchanger). Corrosion can be controlled by polarisation to approximately -0.6 V (vs. Cu/CuSO_4)* and may be achieved using soft iron sacrificial anodes.

Some metals are amphoteric. That is, they form simple cations (in acid solutions) and soluble oxyanions (in alkaline solution); only in the mid-pH range is a protective film stable. Since cathodic protection produces alkali at the structure's surface, it is important to restrict the polarisation, and thereby the amount of hydroxyl ion produced, in these cases. Thus both lead and aluminium will suffer cathodic corrosion under cathodic protection if the potential is made excessively electro negative.

Many passive metals suffer pitting attack when aggressive ions (usually chloride) enter the system. It is possible to forestall pitting, or to stop it once started, using cathodic protection. It is not necessary to polarise to the protection potential of the metal; a negative shift of 100 mV from the natural corrosion potential in the environment will often be sufficient. This technique has been applied to various stainless steels and to aluminium¹⁷. The philosophy is not unlike that applied to rebar in concrete.

Where there is a perceived risk of crevice corrosion, cathodic protection can often be used to prevent its initiation. Once more a 100 mV cathodic polarisation will usually prove sufficient. However, it is doubtful whether cathodic protection can arrest crevice corrosion once started and, despite claims to the contrary, whether it could be effective in arresting stress-corrosion cracking. The problem lies in the fundamental difficulty of forcing cathodic current into an occluded area.

Some recommended protection potentials for other metals are given in Table 10.4.

Steel in Concrete

Concrete is a very benign environment for steel so long as its natural pH remains high and no aggressive species enters. The low corrosion rate experienced by the steel is due to the formation of a protective passive film. There are a number of circumstances that allow chloride ions to enter reinforced concrete. When these ions reach the reinforcing bar (rebar) they may cause localised corrosion damage to it, with consequent cracking, even spalling, of the concrete. The result is both unsightly and potentially dangerous. Impressed current cathodic protection has been used to overcome the problem and significant beneficial effects have been claimed¹³⁻¹⁵.

* In a mixed metal system the protection potential to be adopted is that of the least noble metal, i.e. if the heat exchanger channel had been iron and also required protection, the relevant protection potential would have been -0.85 V vs. Cu/CuSO_4 i.e. the potential relating to steel.

Table 10.4 Recommended protection potentials for other metals^a

<i>Metal</i>	<i>Protection potential</i> (V vs. Cu/CuSO ₄)
Lead	-0.6
Copper-base alloys	-0.5 to -0.65
Aluminium	
+ ve limit	-0.95
- ve limit	-1.2

^a After British Standard Code of Practice CP 1021:1973¹²

The proof of protection is more difficult to establish in this case for two reasons. First, the object is to restore passivity to the rebar and not to render it virtually immune to corrosion. Second, it is difficult to measure the true electrode potential of rebars under these conditions. This is because the cathodic-protection current flowing through the concrete produces a voltage error in the measurements made (see below). For this reason it has been found convenient to use a potential decay technique to assess protection rather than a direct potential measurement. Thus *a 100 mV decay of polarisation in 4 h once current has been interrupted* has been adopted as the criterion for adequate protection¹⁶. It will be seen that this proposal does not differ substantially from the decay criterion included in Table 10.3 and recommended by NACE for assessing the full protection of steel in other environments. Of course, in this case the cathodic polarisation is intended to inhibit pit growth and restore passivity, not to establish effective immunity.

Potential Measurements

It is clear that to ensure adequate protection of a structure under cathodic protection it is necessary to measure its electrode potential. This can only be achieved by using a reference electrode placed in the same environment as the structure and measuring the e.m.f. of the cell so formed. Since the electrode potentials of different types of reference electrode vary, it is clear that the measured e.m.f. will also vary according to the particular reference electrode used. It follows that the potential measured must always be recorded with respect to the reference electrode deployed, which must always be stated.

The protection potential for a given metal is numerically different according to the reference electrode used. Thus the protection potential for iron in aerobic environments is:

- 0.85 V vs. Cu/CuSO₄
- 0.80 V vs. Ag/AgCl/seawater
- 0.77 V vs. Ag/AgCl/1 M KCl
- 0.84 V vs. Ag/AgCl/0.1 M KCl
- 0.55 V vs. standard hydrogen electrode

It is fundamental that a reference electrode should have a stable and reproducible potential. Not all reference electrodes are suitable for all

environments or circumstances. For example a Cu/CuSO_4 electrode is suitable for use in soil, but should never be used in seawater or on concrete. Contamination of the electrode can occur which will produce serious changes in the reference potential.

A Ag/AgCl /seawater electrode should only be used in seawater since the electrode is merely a Ag/AgCl element that provides a known stable reference potential when immersed in clean seawater. Immersion in any other chloride-containing fluid will produce a different reference potential depending on the chloride concentration present in the environment. Only if appropriate allowance is made for the particular chloride content present will the potentials measured be reliable. Commercial Ag/AgCl electrodes are available where the element is encapsulated within an environment containing a fixed chloride content. The electrodes are very stable and suitable for short-term use in fluids containing any concentration of chloride or no chloride ions at all. They are not suitable for continuous immersion in fluids where the chloride concentration of the encapsulation will change with time as a result of chloride leaching (e.g. in distilled water) or chloride ion ingress (e.g. in seawater).

Finally, calomel electrodes (and more especially hydrogen electrodes) are not suitable for field measurements because they are not sufficiently robust. The calomel electrodes are however essential for calibrating the field reference electrodes. Saturated KCl calomel electrodes are the most suitable because there is then no doubt about the reference potential of the calibrating electrode. Lack of adequate calibration is a common cause of cathodic protection system mismanagement.

Incorrect potential measurement technique leads to another management problem. If the potential of a freely corroding metal is measured the values recorded will remain constant wherever the reference electrode is placed in the environment. If the same metal is under cathodic protection the positioning of the reference electrode is crucial. This is because the cathodic protection current flowing through the corrosive environment produces an electric field gradient as the current, I , flows through the environment of resistance, R . Thus, when the reference electrode is placed remote from the metal surface, the measured potential comprises the true electrode potential of the metal and the potential difference in the environment between the metal and the reference electrode due to the electric field. As the reference electrode is moved closer to the metal surface so less of the electric field is included in the measurement and the potential of the metal appears more positive (Fig. 10.9). That is, with current flowing, a remote reference electrode ensures measurement of a more negative potential for the metal (it appears better protected than it is) whilst the closer the reference electrode is placed to the metal the more positive, and more reliable, the measurement becomes.

The deviation from the correct potential value by inclusion of the field gradient in the measurement is often called the IR error and it must be minimised in assessing the state of polarisation of a cathodically protected structure. The recommended protection potentials all assume no significant IR error in the measurement.

It is desirable to measure the potential of a structure without an IR error. It is not always possible to place the reference electrode close to the structure to minimise the IR error but it can be achieved using the so-called

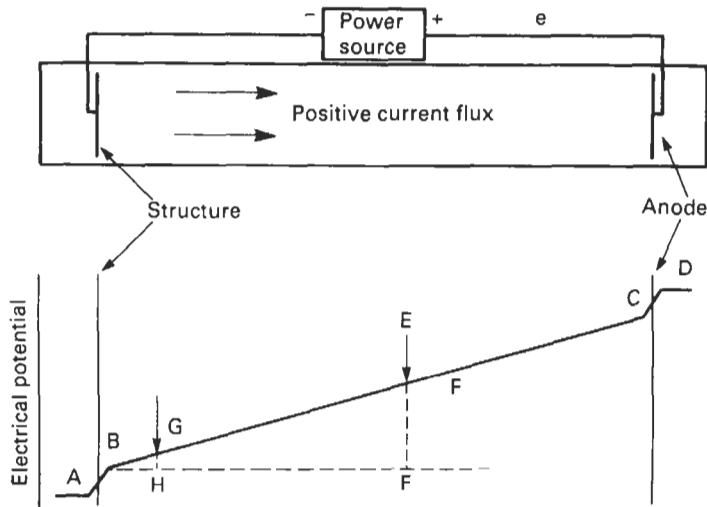


Fig. 10.9 Diagram illustrating the source of the IR error in potential measurements on a cathodically protected structure. BA is the absolute electrode potential of the structure; CD is the absolute electrode potential of the anode; and CB is the field gradient in the environment due to cathodic protection current flux. A reference electrode placed at E will produce an IR error of EF in the potential measurement of the structure potential. If placed at G the error will be reduced to GH . At B there would be no error, but the point is too close to the structure to permit insertion of a reference electrode. If the current is interrupted the field immediately becomes as shown by the dotted line, and no IR is included

instant-off technique. The technique relies on the fact that when the current is interrupted, the IR effect, being ohmic, dissipates immediately but the polarisation decays much more slowly. Thus, if the current is switched off and the potential is measured immediately, the IR -free polarised potential of the structure can be measured. Where the cathodic protection system uses multiple power sources, it is necessary to switch off all the units simultaneously if true IR -free conditions are to be achieved.

In an impressed-current cathodic protection system the power source has a substantial capacity to deliver current and it is possible to change the state of polarisation of the structure by altering that current. Thus effective control of the system depends on credible potential measurements. Since the current output from any given anode is substantial, the possibility of an IR error which may reach many hundreds of millivolts in any potential measurements made is high. Thus the instant-off technique (or some other means of avoiding IR error) is essential to effective system management.

By contrast a cathodic protection system based on sacrificial anodes is designed from the outset to achieve the required protection potential. If this is not achieved in practice there is no control function that can be exercised to improve the situation. Some remodelling of the system will be required. Moreover, the currents from each current source (the sacrificial anodes) is modest so that field gradients in the environment are not significant. It is at once clear that potential measurements are less significant in this case and instant-off measurements are neither necessary nor possible.

Current Requirements

It was indicated earlier that the cathodic current was a poor indicator of adequate protection. Whilst, to a first approximation the protection potential is a function of the metal, the current required for protection is a function of the environment and, more particularly, of the cathodic kinetics it entails. From Fig. 10.4 it is apparent that any circumstance that causes the cathodic kinetics to increase will cause both the corrosion rate and the current required for full (I_c'') or partial ($|I_c'| - I_a'$) protection to rise. For example, an increase in the limiting current in Fig. 10.5 produced by an increase in environmental oxygen concentration or in fluid flow rate will increase the corrosion rate and the cathodic protection current. Similarly, if the environment is made more acid the hydrogen evolution reaction is more likely to be involved in the corrosion reaction and it also becomes easier and faster; this too produces an increased corrosion rate and cathodic current demand.

In short, the current demand for cathodic protection varies according to the aggressiveness of the corrosive environment. It is for this reason that cathodic protection finds its greatest application where the pH is close to neutral. The more acid environments entail a current output that rapidly becomes uneconomic. The more alkaline environments prove less aggressive to the structure and therefore often do not justify cathodic protection. Table 10.5 provides some estimated current densities for cathodic protection that illustrate the point.

Table 10.5 Estimates of the current density required to protect bare steel in various corrosive environments

<i>Environment</i>	<i>Current density (A/m²)</i>
Sulphuric acid (hot, concentrated, stationary)	350–500
Soils	0.01–0.5
Fast-flowing seawater	0.3 ^a
Air-saturated hot water	0.1–0.15
Flowing fresh water	0.05–0.1

^a This value will decay to less than 0.05 A/m² if the calcareous deposit forms.

Coatings and Cathodic Protection

Coatings (e.g. paints) applied to metal surfaces can be extremely effective in containing the corrosion of the substrate in many environments. This is particularly true for steel in natural environments. However, no freshly applied coating is entirely free from defects and so there will always be small areas which are exposed directly to the corrosive environment. It is possible to reduce, but not eliminate, these defects by paying attention to workmanship. In practice, it becomes increasingly expensive to achieve fewer and fewer defects because of the need for high grade inspection, and the detection and repair of individual defects.

Large structures, even in near-neutral pH environments, require a considerable current for cathodic protection. As a result structure coatings are

an almost mandatory requirement when cathodic protection is contemplated. The coating then provides the major part of the protection and the cathodic protection provides the protection at the coating defects. This apparently ideally complementary behaviour occurs because the coating defects represent a low resistance path, and therefore a preferred route, to the structure, for the cathodic protection current. It is now apparent that the coating does not need to achieve total surface coverage and the cathodic protection system must only deliver a fraction (often less than 1%) of the current that would be required to protect a bare structure. Figure 10.10 shows schematically that there is an optimum combination of coating quality and cathodic protection which minimises the cost of protecting a structure.

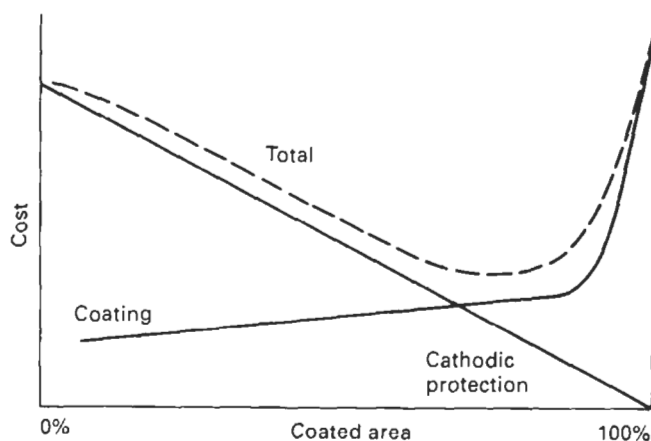


Fig. 10.10 Schematic diagram illustrating the economic benefit of the conjoint use of coating and cathodic protection. The increasing cost of coating as the coating is made progressively more defect free is shown; the corresponding cost of applying cathodic protection to the holidays decreases. The dotted line shows the total cost and that there is overall benefit in using a good coating reinforced by cathodic protection

A coating deteriorates chemically and mechanically during its lifetime. This leads to a progressive increase in both the number of defects and the current required to protect the steel as they occur. Fortunately each new defect represents a new low resistance path and the cathodic protection current will flow to it to provide protection. Of course, this means that the cathodic protection system as installed must have sufficient reserve to provide this necessary extra current. This is readily accommodated in an impressed current system where, if correctly designed, the voltage output can be increased to provide the requisite current. It is rather more difficult in the case of a sacrificial anode system because, as the anodes get smaller (by dissolving sacrificially), they are not capable of delivering more current. Thus increasing current demand develops alongside decreasing current availability. Of course, it is possible to provide anodes capable of delivering substantially more current initially in order to be able to provide sufficient current for later demand. This entails anodes operating in their early

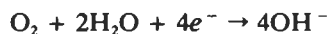
life at low current densities which has sometimes been known to result in anode passivation and failure to deliver any significant current when it is needed.

Notwithstanding this latter difficulty, cathodic protection is usually applied to coated structures. Thus ships, many piers and jetties and virtually all buried pipelines are coated when cathodic protection is applied. Liquid storage tanks standing on sand or bitumen sand often have the underside of their base plate under cathodic protection. Here coating is often omitted, but this is more often due to ignorance of the designer than a conscious decision not to coat. Only offshore oil production platforms, particularly in the North Sea, are cathodically protected but often deliberately uncoated. There are two reasons for this. First, these structures are almost all protected using sacrificial anodes and it is easier to design for a more or less constant current demand than for an increasing current demand in these systems. Second, the construction of the platforms is made against a tight schedule; any weather conditions that prevented completion of coating would involve launching a platform with an incomplete coating and insufficient anodes to protect the now partially coated structure. It is certainly true that the first platforms in the North Sea were coated and cathodically protected. However, at that time the only reliable marine anodes were based on zinc alloys which entailed a heavy weight penalty (because they have a low capacity) and there was thus a pressing need to reduce anode weight by coating. (See also Section 9.4 Design in Marine and Offshore Engineering.)

Calcareous Deposit

It has been noted that the total current required to protect large structures can be substantial even in mildly corrosive environments. In seawater, for example, an initial current in the region of 200 mA/m² for bare steel might well be required in the North Sea. This is because the relatively high oxygen concentration and the tide and wave action all contribute to a facile cathodic reaction. Fortunately this current diminishes with time. The reason for this is the protective scale on the steel surface which forms during cathodic protection by decomposition of the seawater.

During cathodic protection the dissolved oxygen is reduced to produce hydroxyl ions:

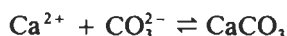


causing an increase in the pH at the interface. Seawater contains carbonate and bicarbonate ions that are in a pH-dependent equilibrium with one another:



The higher the pH of the seawater the greater will be the proportion of carbonate ions present (since as the pH increases, so the H⁺ concentration decreases, thereby moving the equilibrium to the right). It follows that at a surface under cathodic protection, the hydroxyl ion produced has the effect of increasing the local carbonate ion concentration.

Seawater also contains calcium ions which form an insoluble carbonate with carbonate ions:



An increase in carbonate-ion concentration moves the equilibrium in favour of calcium carbonate deposition. Thus one secondary effect of cathodic protection in seawater is the production of OH^- , which favours the production of CO_3^{2-} , which in turn promotes the deposition of CaCO_3 . Cathodically protected surfaces in seawater will often develop an aragonite (CaCO_3) film. This film is commonly referred to as a *calcareous deposit*.

Similarly, the seawater contains magnesium ions which can react with the hydroxyl ion directly to form magnesium hydroxide:



Thus brucite ($\text{Mg}(\text{OH})_2$) is also commonly found on surfaces under cathodic protection in seawater. Because more hydroxyl ions (higher pH) are required to cause magnesium hydroxide to precipitate, the magnesium is virtually always found in the calcareous deposits associated with calcium¹⁸ and its presence is an indicator of a high interfacial pH and thus either high cathodic current densities or relatively poor seawater refreshment.

The practical consequences of these events are that once the calcareous film has formed, a cathodic current density at least an order of magnitude lower than that required to protect bare steel is needed to maintain protection. Although temporary damage to the film (for example, storm action) may create a temporarily increased current demand, the film soon repairs and the lower current demand is restored. There is, however, a danger in excessive cathodic polarisation: hydrogen is evolved at the steel surface which, as it emerges, can itself disrupt the film mechanically. Since the hydrogen continues to be produced so long as there is excessive polarisation, there is continuing mechanical damage to the film and a more or less permanent increase in the cathodic current required for protection.

On the basis of laboratory experiments, it is widely believed, but there is little field evidence to prove, that high initial cathodic current densities promote the development of thinner, more compact and more protective calcareous deposits. If this could be proved some reduction in the sacrificial anode burden on a structure might be possible. As a result some attention has been paid to the possibility of designing cathodic protection systems capable of delivering a high initial current with a view to reducing the total lifetime current required to attain and maintain protection. In general, this approach has involved proposals to use a limited number of high-current output magnesium alloy sacrificial anodes to reinforce the anode burden (usually aluminium alloy) installed to provide long term protection. It remains to be seen whether this is, or could be, successful.

Potential Attenuation in Impressed-current Systems

An impressed-current cathodic protection system circuit comprises an anode, the power source, the structure and the environment in which it

is placed. In addition, there are electrical connections between the power source and the anode and between the power source and the structure (at the so-called negative drain point). The voltage available from the power source is used to polarise the anode and the structure and to overcome the electrical resistance of the environment and the metallic circuit, including that of the structure itself. It follows that the overall circuit resistance to various parts of a very large structure will differ and that, where the resistance is higher, the voltage available for polarisation of the structure will be lower. Thus on large structures protected by a limited number of anodes, some lateral variation in the level of polarisation is to be expected. This variation of potential is referred to as *attenuation*. Given that to ensure full protection the structure should everywhere be polarised at least to the protection potential, some part of it must be polarised to a greater extent. We have seen that more polarisation requires more cathodic current. In the interest of economy it is important to minimise attenuation as far as possible. One practical way to achieve this is to use a protective coating and so limit the total current in the circuit. It may then still prove desirable to use more than one anode groundbed* to render the attenuation less extreme. To pursue this latter course it is helpful to have some assessment of the likely level of attenuation that will be experienced on a given structure.

No exact mathematical analysis of potential attenuation for all structures has yet been developed. Some indicative analysis has been achieved for a buried pipeline¹⁹ which is perhaps the simplest case.

In making the analysis it is assumed that the anode groundbed is remote from the pipeline. That is, the length of the pipeline in question stands in what is virtually a uniform anode field, as shown in Fig. 10.11. Since the

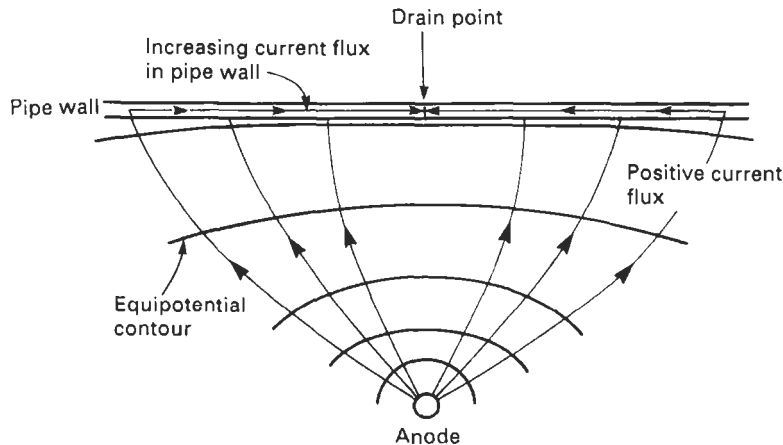


Fig. 10.11 Schematic diagram showing an impressed-current anode installed in a groundbed remote from a pipeline. The positive current produces a field gradient in the soil, but the gradient tends to zero close to the line producing a uniform lateral electrical potential on the soil side

* An anode buried in the ground or soil.

electrical potential on the soil side is constant, any electrical potential change in the pipeline metal due to current flow within it reflects an equal electrode potential change at the pipe-soil interface. The change is also numerically equal to the cathodic overpotential, i.e. the shift in electrode potential from the spontaneous corrosion potential.

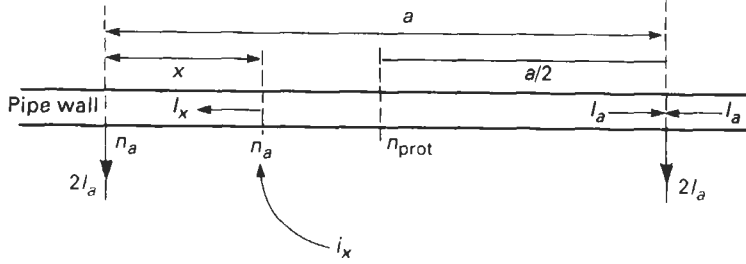


Fig. 10.12 Schematic representation of a pipewall subject to cathodic protection (see text). η_x = overpotential at x ; η_a = overpotential at $x = 0$; η_{prot} = overpotential at $x = a/2$; I_x = current line at x ; i_x = current density entering line at x ; i_a = current in line at $x = 0$ from one side of drain point ($2i_a$ = total current drain); a = distance between the drain points

We assume that the current enters the pipeline from the soil side through defects in the coating and returns to the power source via the line and one of the drain points, as shown in Fig. 10.12. If the total current in the pipeline at a point a distance x from a drain point is I_x , then the change in current per unit length at x is the current entering at x :

$$\frac{dI_x}{dx} = -2\pi r i_x \quad (10.5)$$

where r is the radius of the pipeline and i_x the current density entering at x .

The electrical potential change along the pipeline at x is

$$\frac{d\phi_x}{dx} = -R_L I_x$$

where ϕ_x is the electrical potential at x and R_L the resistance of the metallic pipeline/unit length. However, since the rate of electrical potential change is equal to the rate of change of overpotential, given a remote grounded, it follows that:

$$\frac{d\eta_x}{dx} = -R_L I_x \quad (10.6)$$

where η_x is the overpotential and is the difference between the actual potential at x and the free corrosion potential of the metal.

From equations 10.5 and 10.6:

$$\frac{d^2\eta_x}{dx^2} = R_L (2\pi r i_x) \quad (10.7)$$

Now, when i_x is small, the polarisation of the pipeline is approximately directly proportional to the true current density (i'_x) at the holidays (Section 10.7, page 10:149) in the coating. Thus

$$\eta_x = k' i'_x \quad (10.8)$$

Also,

$$i'_x = \frac{i_x}{f}$$

where f is the fraction of the surface covered by holidays in the coating and is inversely proportional to the resistance of the coating/unit area (z).

Thus

$$\eta_x = k' i'_x = \frac{k' i_x}{f} = K i_x z \quad (10.9)$$

where K is a constant that depends on the nature of the structure to be protected and the properties of the soil.

From equations 10.7 and 10.9:

$$\frac{d^2 \eta_x}{dx^2} = R_L \left(\frac{2\pi r}{Kz} \right) \eta_x \quad (10.10)$$

The solution to equation 10.10 for an infinite pipeline, i.e. when $\eta_x = 0$, $x = \infty$ and when $\eta_x = \eta_a$, $x = 0$, is:

$$\eta_x = \eta_a \exp \left[- \left(\frac{2\pi r R_L}{Kz} \right)^{\frac{1}{2}} x \right] \quad (10.11)$$

However, if the pipeline has multiple drain points separated by distance ' a ' and the aim is that the pipeline electrode potential should just reach the protection potential at the mid-point ($x = a/2$), then $\eta_{x=a/2}$ is equal to η_{prot} (the overpotential required just to achieve the protection potential). At $x = a/2$ the current in the line is zero and $(d\eta_x/dx)_{x=a/2}$ is also zero. Thus:

$$\eta_x = \eta_{\text{prot}} \cdot \cosh \left[\left(\frac{2\pi r R_L}{Kz} \right)^{\frac{1}{2}} \left(x - \frac{a}{2} \right) \right] \quad (10.12)$$

and

$$\eta_a = \eta_{\text{prot}} \cdot \cosh \left[- \left(\frac{2\pi r R_L}{Kz} \right)^{\frac{1}{2}} \frac{a}{2} \right] \quad (10.12a)$$

The current in an infinite pipeline is obtained by differentiating equation 10.11 and substituting into equation 10.6:

$$I_x = \left(\frac{2\pi r R_L}{Kz} \right)^{\frac{1}{2}} \frac{\eta_a}{R_L} \cdot \exp \left[- \left(\frac{2\pi r R_L}{Kz} \right)^{\frac{1}{2}} x \right] \quad (10.13)$$

The drainage current (i.e. $(2I_{x=0})$) is therefore:

$$2 \cdot \left(\frac{2\pi r R_L}{K_z} \right)^{\frac{1}{2}} \frac{\eta_a}{R_L} \quad (10.13a)$$

This analysis is far from exact since it assumes a remote grounded, uniform soil resistivity and uniform defect density in the coating. At best it demonstrates that attenuation is likely to follow an exponential decay and that it will be less severe for larger diameter pipes than for smaller. The problem is more difficult to solve for more complex structures (e.g. congested pipeline networks) and especially so for marine installations where the development of the calcareous deposit introduces the possibility of temporal variations in attenuation.

The question of attenuation is not significant in the case of sacrificial anode protection systems where the individual source outputs are small.

Summary

Cathodic protection is a long established and proven technique for protecting metals from corrosion. Whilst in principle it may be used to protect any metal in an aqueous environment, in practice it is used mainly to protect carbon steels in natural environments such as water, soil and sand. Other metals often do not require protection because they do not corrode significantly under these circumstances. More aggressive environments render cathodic protection less attractive because of the substantial cost of providing the requisite current. Nevertheless, cathodic protection is applied to a vast area of metal on structures such as buried pipelines, ships, piers and jetties, oil production platforms and liquid storage tanks. More recently the protection of reinforcing bar in concrete has received attention. Cathodic protection is therefore of great technological significance.

There are two methods of applying cathodic protection, viz using an impressed current or a sacrificial anode. The former requires a source of d.c. power, but is then capable of delivering large voltages (< 100 V) and currents (< 100 A). A sacrificial anode operates independently of a source of d.c. power but only delivers a voltage of about 1 V and a current that will rarely exceed 5 A. The relative advantages of the two methods largely derive from these differences.

Cathodic protection benefits from its conjoint use with a coating on the structure; the current required for protection is reduced. However, in seawater the application of the technique encourages deposition of protective salts which to some extent achieves the same objective.

Since cathodic protection, if operated correctly, can prevent the corrosion of a metal entirely, it is unique amongst all the methods of corrosion control.

V. ASHWORTH

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10.2 Sacrificial Anodes

Introduction

This chapter is intended as an introduction and guide to the use of sacrificial anodes for cathodic protection.

After considering the principles of operation and application of sacrificial anodes the basic terminology encountered when dealing with sacrificial anodes is presented. A systematic approach takes the reader through the requirements of anode materials and goes on to cover the factors affecting their performance and those areas important to the selection of anode materials. The chapter concludes by detailing considerations for the design of sacrificial anode systems.

Principles of Operation

The thermodynamic and electrode-kinetic principles of cathodic protection have been discussed at some length in Section 10.1. It has been shown that, if electrons are supplied to the metal/electrolyte solution interface, the rate of the cathodic reaction is increased whilst the rate of the anodic reaction is decreased. Thus, corrosion is reduced. Concomitantly, the electrode potential of the metal becomes more negative. Corrosion may be prevented entirely if the rate of electron supply is such that the potential of the metal is lowered to the value where it is found that anodic dissolution does not occur. This may not necessarily be the potential at which dissolution is thermodynamically impossible.

When two different metals are immersed in the same electrolyte solution they will usually exhibit different electrode potentials. If they are then connected by an electronic conductor there will be a tendency for the potentials of the two metals to move towards one another; they are said to mutually polarise. The polarisation will be accompanied by a flow of ionic current through the solution from the more negative metal (the anode) to the more positive metal (the cathode), and electrons will be transferred through the conductor from the anode to the cathode. Thus the cathode will benefit from the supply of electrons, in that it will dissolve at a reduced rate. It is said to be 'cathodically protected'. Conversely, in supplying electrons to the cathode the anode will be consumed more rapidly, and thus will act as a sacrificial anode.

It follows from the above that, for an anode material to offer sacrificial protection, it must have an open-circuit potential that is more negative than that of the structure itself (the cathode). The extent of protection experienced by the cathode will depend on the potential it achieves. This is dependent on the electrochemical properties of the anode which in turn are governed by its composition and the environment to which it is exposed.

Applications of Sacrificial Anodes

Examples of the application of sacrificial anodes include the following: ships' hulls¹, offshore oil and gas drilling rigs, production platforms/semi-submersibles and support facilities^{2,3}, underwater pipelines, underground pipelines⁴, buried structures, harbour piling and jetties⁵, floating docks, dolphins, buoys, lock gates and submerged concrete structures⁶. There are many other uses, including a large range of industrial equipment where the surfaces are in contact with corrosive electrolytes, e.g. heat exchangers, pump impellers and vessel internals.

Sacrificial Anode Basics

Anode Operating Potential, Protection Potential and Driving Voltage

The operating potential of an anode material is its potential when coupled to a structure (i.e. the closed-circuit potential). Since all commercial anode materials are formulated to suffer only slight polarisation under most conditions of exposure, the operating potential approximates to the open-circuit potential. Indeed, any substantial difference (> 50 mV) between these two potentials will call into question the suitability of the anode in the particular environment.

The protection potential refers to the potential at which experience shows corrosion of a metal will cease. Different materials have different protection potentials (Table 10.6). Occasionally a less negative protection potential will be specified because some degree of corrosion is permissible. It should be noted that in a mixed metal system the protection potential for the most base metal is adopted.

Table 10.6 Protection potentials of metals in seawater (V vs. Ag/AgCl/seawater)

Iron and steel	
aerobic environment	-0.8
anaerobic environment	-0.9
Lead	-0.55
Copper alloys	-0.45 to -0.60

The driving voltage is the difference between the anode operating potential and the potential of the polarised structure to which it is connected. For design purposes, the driving voltage is taken as the difference between the anode operating potential and the required protection potential of the structure.

Anode Capacity and Anode Efficiency

The *anode capacity* is the total coulombic charge (current \times time) produced by unit mass of an anode as a result of electrochemical dissolution. It is normally expressed in ampere hours per kilogram (Ah/kg) although the inverse of anode capacity, i.e. the *consumption rate* (kg/Ay) is sometimes used.

The theoretical anode capacity can be calculated according to Faraday's law. From this it can be shown that 1 kg of aluminium should provide 2981 Ah of charge. In practice, the realisable capacity of the anode is less than the theoretical value. The significance of the actual (as opposed to the theoretical) anode capacity is that it is a measure of the amount of cathodic current an anode can give. Since anode capacity varies amongst anode materials, it is the parameter against which the anode cost per unit anode weight should be evaluated.

The anode efficiency is the percentage of the theoretical anode capacity that is achieved in practice:

$$\text{anode efficiency} = \frac{\text{anode capacity}}{\text{theoretical capacity}} \times 100\%$$

Anode efficiency is of little practical significance and can be misleading. For example, magnesium alloy anodes often have an efficiency ca. 50% whilst for zinc alloys the value exceeds 90%; it does not follow that zinc alloy anodes are superior to those based on magnesium. Efficiency will be encountered in many texts on sacrificial anode cathodic protection.

Anode Requirements

The fundamental requirements of a sacrificial anode are to impart sufficient cathodic protection to a structure economically and predictably over a defined period, and to eliminate, or reduce to an acceptable level, corrosion that would otherwise take place.

In view of the above criteria, the following properties are pre-requisites for the commercial viability of a sacrificial anode:

1. The anode material must provide a driving voltage sufficiently large to drive adequate current to enable effective cathodic polarisation of the structure. This requirement implies that the anode must have an operating potential that is more negative than the structure material to be protected.
2. The anode material must have a more or less constant operating potential over a range of current outputs. Consequently the anode must resist polarisation when current flows; the polarisation characteristics must also be predictable.
3. An anode material must have a high, reproducible and available capacity, i.e. whilst acting as an anode, it must be capable of delivering consistently and on demand a large number of ampere hours per kilogram of material spent. The ideal anode material will not passivate in the exposure environment, will corrode uniformly thus avoiding

mechanical fragmentation (hence wastage), and will approach its theoretical capacity.

4. The production of large quantities of alloy material in anode form, and possessing the desired mechanical properties, must obviously be practicable and economic. Thus secondary processing such as heat treatment is undesirable.

Sacrificial Anode Materials

Whilst cathodic protection can be used to protect most metals from aqueous corrosion, it is most commonly applied to carbon steel in natural environments (waters, soils and sands). In a cathodic protection system the sacrificial anode must be more electronegative than the structure. There is, therefore, a limited range of suitable materials available to protect carbon steel. The range is further restricted by the fact that the most electronegative metals (Li, Na and K) corrode extremely rapidly in aqueous environments. Thus, only magnesium, aluminium and zinc are viable possibilities. These metals form the basis of the three generic types of sacrificial anode.

In practice, with one minor exception (pure zinc), the commercially pure metals are unsuitable as sacrificial anode materials. This is because they fail to meet one or more of the pre-requisites outlined above. In each generic type of material alloying elements are added to ensure more acceptable properties.

Table 10.7 provides a list of the more important anode materials by broad category, and some indication of their operating parameters. It is at once, clear that there are major differences in performance between one generic type and another. Thus the magnesium alloys have very negative operating potentials and are therefore able to provide a large driving voltage for cathodic protection; zinc and aluminium alloys are more modest in this respect. Aluminium alloys, by contrast, provide a substantial current capacity which is more than twice that available from the zinc and magnesium alloys. It might appear that this implies that if the driving voltage is the most important feature in a given cathodic protection system (e.g. when there is a need for short-term high currents or a high resistivity to overcome) then magnesium alloys are to be preferred, but if a high capacity is required (e.g. steady delivery of current over a long life) aluminium alloys would be better. In practice, selection is significantly more complicated and the topic is discussed in more detail in later sections.

Table 10.7 Anode potentials of various alloys used for cathodic protection

<i>Alloy</i>	<i>Anode potential (V vs. Ag/AgCl/Seawater)</i>	<i>Max current capacity (Ah/kg)</i>
A-Zn-Hg	-1.0 to -1.05	2 830
A-Zn-Sn	-1.0 to -1.10	2 600
A-Zn-In	-1.0 to -1.15	2 700
Zn-Al-Cd	-1.05	780
Mg-Mn	-1.7	1 230
Mg-A-Zn	-1.5	1 230

Even within a generic type of alloy there are significant performance differences. Thus, for example, Al-Zn-In alloys provide a higher driving voltage but a lower current capacity than Al-Zn-Hg alloys. Once a decision to use a generic type of alloy has been made, these apparently small differences in performance become important in the final selection. This subject is also discussed below.

Alloying additions are made to improve the performance of an anode material. Of equal importance is the control of the levels of impurity in the final anode, since impurities (notably iron and copper) can adversely affect anode performance. Thus careful quality control of the raw materials used and the manufacturing process adopted is essential to sound anode production. This too is discussed below.

An intimate knowledge of the factors influencing the operation of sacrificial anodes and design parameters, is essential if a full appreciation of how best to select an anode and achievement of optimum performance is to be realised. The following considerations deal with those factors which ultimately determine anode performance.

Factors Affecting Anode Performance

Alloy Composition

The constituent elements of anode materials, other than the basis metal, are present whether as a result of being impurities in the raw materials or deliberate alloying additions. The impurity elements can be deleterious to anode performance, thus it is necessary to control the quality of the input materials in order to achieve the required anode performance. Since this will usually have an adverse impact on costs it is often desirable to tolerate a level of impurities and to overcome their action by making alloying additions. Alloying elements may also be added for other reasons which are important to anode production and performance. These matters are discussed in this section.

In general, sacrificial anode alloy formulations are proprietary and covered by patents. The patent documents are often very imprecise where they relate to compositions that will produce effective anodes and quite inaccurate in ascribing the function to a given alloying element. Whilst the commercial literature is more specific where it relates to compositions, it rarely details the purpose of an alloying addition. In discussing alloy composition here, the treatment derives from the technical literature and can only be a broad-brush account. This is because the laboratory work reported in the literature has tended to be more empirical than scientific, being directed towards producing viable anodes.

Impurities

Zinc is relatively low in the electrochemical series and is widely regarded as an active metal. However, when high-purity zinc is placed in hydrochloric acid it will dissolve extremely slowly, if at all. It may be encouraged to

dissolve by placing it in contact with platinum metal. Hydrogen evolution will occur vigorously on the platinum and the zinc will dissolve freely. Zinc proves to be a poor cathode for hydrogen evolution and cannot, therefore, easily support the cathodic reaction that would lead to its own corrosion. The platinum provides the surface on which this cathodic reaction easily occurs. If, by contrast, the zinc is of commercial quality it will dissolve readily in the acid. This is because the impurities in the zinc provide the cathodic sites for hydrogen evolution which allows the zinc to corrode.

One important feature of an anode alloy is that it should dissolve with a capacity approaching the theoretical value. That is, all the electrons released by the metal dissolving should be transferred to the structure to support the cathodic reaction there, and should not be wasted in local cathodic reactions on its own surface. In other words an anode should act like the pure zinc described above (i.e. only dissolve when attached to a good cathode) rather than impure zinc.

In all the generic types of sacrificial anode alloys the presence of iron is found to be deleterious. This is because an intermetallic compound formed between it and the basis metal proves to be a good cathode. Its presence will result in a substantial lowering of the capacity of an anode. Moreover, the presence of this cathodic material will often raise (make less negative) the anode operating potential and may, in the limit, promote actual passivation. Thus the driving force available from the anode is reduced or completely destroyed. For example, when the solid solubility of iron in zinc (ca. 14 ppm) is exceeded the anode operating potential becomes more positive. This has been attributed to the formation of $\text{Zn}(\text{OH})_2$, around intermetallic precipitates of FeZn_{13} ⁷. The presence of iron has a similar adverse effect in aluminium⁸ and magnesium alloys⁹.

There are two ways of avoiding the iron problem: to control the iron added with the basis metal or to sequester the iron in some way to render it ineffective. In practice it is not possible to permit more than a limited iron content because sequestering is only economic and practicable within defined limits.

It has been seen that iron has an adverse effect because it forms a second phase (insoluble) material in the alloy which acts as an effective local cathode. Sequestering is the technique of adding an alloying addition that will cause an alternative intermetallic compound with iron to form. This compound might form a dross to be removed mechanically. Alternatively the new intermetallic compound could be a less effective cathode in which case removal would not be necessary.

Both silicon and aluminium are added to zinc to control the adverse effects of iron. The former forms a ferro-silicon dross⁷ (which may be removed during casting). Aluminium forms an intermetallic compound which is less active as a cathode than FeZn_{13} ⁷. Similarly in aluminium and magnesium alloys, manganese is added to control the iron^{8,9}. Thus in aluminium alloys for example, the cathodic activity of, FeAl_3 is avoided by transformation of FeAl_3 to $(\text{Fe}, \text{Mn})\text{Al}_6$ ⁸. This material is believed to have a corrosion potential close to that of the matrix and is, therefore, unable to produce significant cathodic activity¹⁰.

There will be an upper limit on the level of impurity that can be overcome by alloying additions. The addition of manganese is not effective in

Al-Zn-In alloys if the iron content exceeds 0.22%⁸. Equally there may be a limit on the level of alloying addition. This may be related to the absolute level of alloying addition present or to the permissible ratio between it and the impurity element. For example, as Fig. 10.13 shows, a progressive increase in the Mn:Fe ratio in an Al-Zn-In anode increases the capacity quite markedly, but once the 1:1 ratio is reached an even more dramatic fall is found.

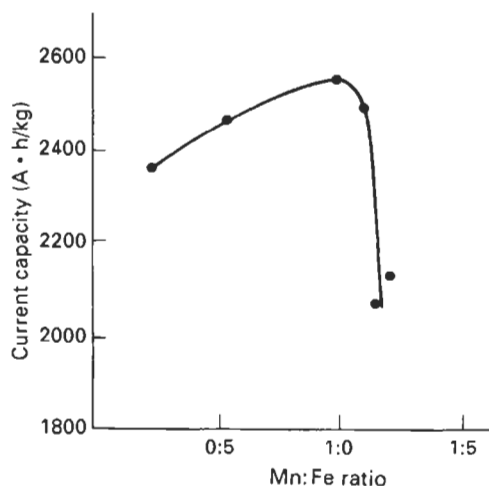


Fig. 10.13 The effect of the Mn/Fe ratio on the performance of Al-Zn-In-Mn anode alloys. Alloy composition range: Zn 4.0–4.6%; In 0.020–0.029%; Mn 0.004–0.35%; Fe 0.06–0.30% (after Klinghoffer and Linder⁸)

Other heavy metal impurities (especially copper and nickel) have similar adverse effects on all generic alloy types. In their case sequestering has not proved successful and control of input quality is used to keep their concentration acceptably low⁹.

Table 10.8 outlines the quality requirements of the basis, or primary, metal for the three generic types of anode. These are the qualities required even when sequestering is also adopted. It will be seen that two grades are listed in the case of aluminium. This is because certain patented formulations permit the lower (99.8%) grade material providing that the iron and silicon are within the limit given.

Alloying Additions

We have seen that the adverse effect of impurities can, within limits, be controlled by alloying additions. Thus silicon and aluminium are added to zinc, and manganese to aluminium and magnesium, to counter the effect of iron.

Additions are made for other purposes, all of which aim to improve the performance of the anode. These include lowering the anode operating

Table 10.8 Suitable primary material quality requirements

99·90% Magnesium			99·99% Zinc		
Cu	0·02	max	Pb	0·003	max
Mn	0·01	max	Cu	0·001	max
Sn	0·01	max	Cd	0·003	max
Ni	0·001	max	Fe	0·002	max
Pb	0·01	max	Sn	0·001	max
others	0·05	max	Zn	99·99	min
Mg	99·90	min			
99·80% Aluminium			99·99% Aluminium		
Fe	0·12	max	Pb	0·003	max
Si	0·08	max	Cu	0·002	max
Cu	0·03	max	Cd	0·003	max
Zn	0·03	max	Fe	0·003	max
Mn	0·02	max	Sn	0·001	max
Mg	0·02	max	Al	99·99	min
Al	99·80	min			

potential to increase the driving voltage, avoiding passivation, increasing the anode capacity, improving the dissolution morphology, modifying the mechanical properties of the dissolution product to promote detachment, and improving the mechanical properties of the anode.

Table 10.9 lists some common zinc anode alloys. In three cases aluminium is added to improve the uniformity of dissolution and thereby reduce the risk of mechanical detachment of undissolved anode material⁹. Cadmium is added to encourage the formation of a soft corrosion product that readily crumbles and falls away so that it cannot accumulate to hinder dissolution⁷. The Military Specification material was developed to avoid the alloy passivating as a result of the presence of iron⁹. It later became apparent that this material suffered intergranular decohesion at elevated temperatures (>50°C) with the result that the material failed by fragmentation¹¹. The material specified by Det Norske Veritas was developed to overcome the problem: the aluminium level was reduced under the mistaken impression that it produced the problem. It has since been shown that decohesion is due to a hydrogen embrittlement mechanism¹⁴ and that it can be overcome by the addition of small concentrations of titanium¹⁵. It is not clear whether

Table 10.9 Standard zinc alloys

<i>Alloy component (wt%)</i>	<i>ASTM B418-88 Type I</i>	<i>ASTM B418-88 Type II</i>	<i>US Mil¹² Spec. A 18001 J</i>	<i>DnV Recomm¹³ for elevated temp.</i>
Al	0·10-0·50	0·005 max	0·10 -0·50	0·10-0·20
Cd	0·025-0·07	0·003 max	0·025-0·07	0·03-0·06
Fe	0·005 max	0·0014 max	0·005 max	0·002 max
Cu	0·005 max	0·002 max	0·005 max	0·005 max
Pb	0·006 max	0·003 max	0·006 max	0·006 max
Si	—	—	—	0·125 max
Others (total)	0·1	—	0·10	—
Zn	remainder	remainder	remainder	remainder
Operating potential (V vs. Ag/AgCl/seawater)	-1·05	-1·05	-1·05	-1·05
Capacity (Ah/kg)	780	780	780	780

the titanium acts as a getter for hydrogen or simply serves to refine the grains and increase the grain boundary area thereby diluting the embrittlement effect. It is claimed that newly developed alloys with magnesium additions are also resistant to intergranular attack at elevated temperatures^{9,11}.

Although aluminium is a base metal, it spontaneously forms a highly protective oxide film in most aqueous environments, i.e. it passivates. In consequence, it has a relatively noble corrosion potential and is then unable to act as an anode to steel. Low level mercury, indium or tin additions have been shown to be effective in lowering (i.e. making more negative) the potential of the aluminium; they act as activators (depassivators). Each element has been shown to be more effective with the simultaneous addition of zinc¹⁶. Zinc additions of up to 5% lower the anode operating potential, but above this level no benefit is gained⁷. Below 0.9% zinc there is little influence on the performance of aluminium anodes⁹. Table 10.10 lists a number of the more common commercial alloys.

Table 10.10 Proprietary aluminium anode materials

<i>Alloy component (wt%)</i>	<i>Al-Zn-In</i>	<i>Al-Zn-In(-Mn-Mg)¹⁷</i>	<i>Al-Zn-Sn</i>	<i>Al-Zn-Hg</i>
Fe	0.12 max	0.18 max	0.13 max	0.08 max
Si	0.05-0.20	0.01-0.02	—	0.11-0.21
Zn	2.8-6.5	2.0-6.0	4.0-5.0	0.35-0.50
Hg	—	—	—	0.35-0.50
In	0.01-0.02	0.01-0.03	—	—
Sn	—	—	0.1	—
Mg	—	0.1-2.0	—	—
Cu	0.006 max	0.01 max	0.01 max	0.006 max
Mn	—	0.1-0.2	—	—
Ti	—	0.02 max	—	—
Others (each)	0.02 max	—	—	—
Al	remainder	remainder	remainder	remainder
Operating Potential (V vs Ag/AgCl/seawater)	-1.10	-1.10	-1.10	-1.05
Capacity (Ah/kg)	2 700 max	2 700 max	variable	2 830 max

The best capacities in seawater are obtained from alloys containing zinc and mercury, but this is achieved at the expense of a somewhat more noble operating potential. Zinc and indium additions give a less noble operating potential but are associated with a lower capacity. In practice this effect on the operating potential can be quite significant. The driving voltage between Al-Zn-Hg (operating potential -1.05 V) and steel (protection potential -0.80 V) is 0.25 V. The use of Al-Zn-In provides a 20% increase in driving voltage and thereby the possibility of a higher current output. Thus, both alloys have important advantages and disadvantages. However, the toxic nature of mercury may prohibit its use in rivers or harbour waters.

The Al-Zn-Sn alloys require careful heat treatment in their production. Inevitably this leads to more expense and inconvenience. The advent of the alloys containing mercury or indium rendered these alloys very much less attractive. Presently Al-Zn-Hg alloys are under some pressure because

of the toxicity of mercury. As a result there has been a decline in their use as compared with the Al-Zn-In alloys.

Improved capacity has been reported in saline mud environments by making magnesium additions (0.1–2.0%) to Al-Zn-In alloys¹⁷. These materials can age harden and hence suffer reduced ductility. Since this can subsequently lead to longitudinal cracking of the anodes they should not be cast in thin sections¹⁸. Higher levels (up to 8%), whilst improving strength and casting characteristics, incur the disadvantage of a reduced capacity⁹.

Both titanium and boron can be added as grain refiners to ensure small grain size and hence high surface area grain boundaries¹⁹. This reduces the risk of preferential attack at grain boundaries and promotes more uniform dissolution.

Typical proprietary magnesium anode materials are given in Table 10.11. Magnesium anodes comprise two distinct types, the Mg-Mn and Mg-Al-Zn alloy systems. Additions of up to 1.5% manganese to high-purity magnesium yields a material with an operating potential of -1.7 V vs. Ag/AgCl/seawater. The Mg-Mn alloys therefore exhibit very high driving potential and thus find application in particularly resistive environments. Mg-Al-Zn anodes have an operating potential (-1.5 V vs. Ag/AgCl/seawater) 200 mV above that of the Mg-Mn alloys. This is very favourable in view of problems with overprotection. Thus they are more popular in typical environments than the Mg-Mn alloys. The alloys also contain manganese which is added to overcome the deleterious effects of iron⁹. Alloying additions of aluminium, zinc and manganese to magnesium serve to improve the anode capacity and reduce the operating potential, compared with that of pure magnesium⁹. There is however no difference between the capacity of Mg-Mn and Mg-Al-Zn anodes.

Table 10.11 Proprietary magnesium alloys

	Mg-Mn No. 1	Mg-Mn No. 2	Mg-Al-Zn
Cu	0.02	0.02 max	0.08 max
Al	0.01 max	0.05 max	5.3–6.7
Si	—	0.05 max	0.3 max
Fe	0.03	0.03 max	0.005 max
Mn	0.5–1.3	0.5–1.5	0.25 min
Ni	0.001	—	0.003 max
Zn	—	0.03 max	2.5–3.5
Others (each)	0.01 max	0.03 max	0.03 max
Mg	remainder	remainder	remainder
Operating potential (V vs. Ag/AgCl/seawater)	-1.7	-1.7	-1.5
Capacity (Ah/kg)	1 230	1 230	1 230

Many more exotic compositions for anode materials are often encountered in the literature. It should be appreciated, however, that continual mention in texts of these materials in no way reflects their usage or acceptance commercially as viable sacrificial anodes.

Metallurgical Factors

In producing anodes, the production method must not compromise the benefits of alloy formulation. A number of undesirable anomalies can occur during production which may detract from the desired anode properties. Some of these are discussed below. A detailed account of production requirements can be found elsewhere²⁰.

Although most anodes are made by gravity casting, some are made by continuous casting or extrusion. The method of casting affects the physical structure of the anode. That is, the associated cooling process will influence the segregation of alloying constituents. In some cases it is undesirable to permit segregation since this may lead to preferential attack at grain boundaries. However, it is believed that segregation of activating elements by inverse segregation benefits the performance of some alloys. This mechanism is a suggested explanation for the mercury- and indium-rich phases found on the surfaces of aluminium anodes¹⁵. The increased surface concentrations of these elements aid activation and are therefore beneficial.

Porosity within the anode is detrimental since the weight of anode material, and hence the number of ampere hours of charge unit mass available will be less for a given shape. Moreover, it is possible that hydrolysis of dissolution products will occur in the pores. This leads to local acidity and a reduction in capacity. Necking of the interconnecting pore walls during dissolution may also result in the loss of intact anode material by fragmentation, thus reducing the anode capacity further. The inclusion of extraneous matter, as a consequence of unclean foundry practices may likewise increase the tendency to fragmentation.

Cracking of anodes during casting is in many cases unavoidable due to the stresses imposed by cooling. The problem is more common in Al-Zn-Hg anodes and less common when continuous casting is used. Longitudinal cracks cannot be accepted as these will lead eventually to mechanical loss of material. A greater tolerance to transverse cracks can be exercised. For example, one quality specification permits an anode completely supported by the insert to have transverse cracks of unlimited length and depth provided that there are no more than ten cracks per anode and their width does not exceed 5 mm²⁰. This is somewhat arbitrary but emphasises the point that cracks which threaten anode integrity are of more importance than those which lead to reduced performance.

The anode material must stay firmly attached to the steel insert, which is necessary to conduct the current from the anode to the structure, throughout its design life to remain effective. Consequently surface preparation (by dry blast cleaning²⁰) of the insert prior to casting, to ensure a sound bond with the anode material, is essential. Voids at the insert/anode material interface are undesirable as these will also affect the bond integrity.

Environmental Factors

The conditions of environmental exposure play a key role in determining anode performance. Indeed, specific environments often preclude, or necessitate, the use of particular anode materials.

This section is not intended to deal with those environmental factors which influence cathodic current demand (e.g. oxygen availability or the presence of calcareous deposits) but those which directly affect the performance of the anodes.

Temperature is of particular importance to the performance of anodes, especially when anodes are buried. Anodes may often be used to protect pipelines containing hot products. Thus temperature effects must be considered. Figure 10.14 illustrates the effect of temperature on different anodes in hot saline mud. Al-Zn-In anodes experience greatly reduced capacity in open seawater at temperatures above 70°C ²¹ (down to 1200 Ah/kg at 100°C) and in seabed muds in excess of 50°C ^{21,22} (900 Ah/kg at 80°C). At elevated temperatures passivation of both aluminium alloys and pure zinc can occur²³. Considerable improvement in performance (capacity, and to a lesser extent operating potential) has been claimed for a range of modified Al-Zn-In anode materials¹⁷.

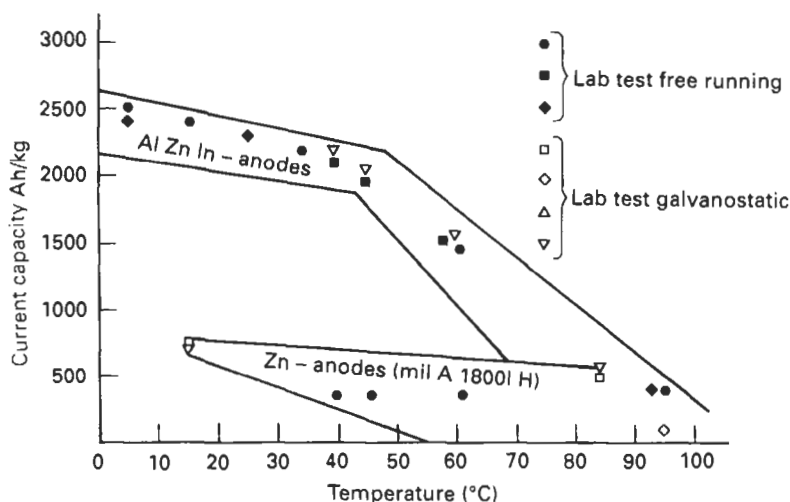


Fig. 10.14 Capacity-temperature relationships for anodes covered with saline mud (after Jensen and Torleif¹¹)

Zinc anodes have also experienced problems at elevated temperatures in saline mud, suffering intergranular decohesion at approximately 70°C ²⁴. Later work by the same authors showed the threshold for damage to be ca. 50°C . The material is not recommended above 40°C ¹¹ although special zinc based materials for temperatures exceeding 50°C have been developed¹³ (1993). Pure zinc, which does not suffer intergranular decohesion, will passivate under these conditions¹¹. It is claimed that newly developed Zn-Al-Mg anodes will perform satisfactorily at elevated temperatures¹¹. Nevertheless Al-Zn-In anodes have been specified for operation above 50°C ¹¹. Further-

more, steps are now taken to ensure that the anode design prevents anode material being exposed to elevated temperatures under buried conditions.

The presence of H_2S (from bacterial activity in anaerobic saline mud, for example) can result in a significant decrease (16%) in capacity and loss of operating potential for Al-Zn-In anodes²².

Environmental resistivity and chloride content will affect anode performance. Aluminium alloy anodes require the presence of chloride ions to prevent passivation. Land-based applications generally provide insufficient chloride levels for this purpose. Consequently aluminium alloy anodes only find application in saline environments. The capacity and operating potential, of aluminium alloy anodes in particular, illustrated in Figs. 10.15 and 10.16, are dependent on the degree of salinity. With reducing salinity the anode capacity will decrease and the operating potential rise. This becomes increasingly significant below 10–20% seawater strength and is important for design in estuarine conditions. Passivation of aluminium alloy anodes as a consequence of electrolyte stagnation may occur, particularly if the anode is immersed in silt or sand; zinc performs reasonably under these conditions.

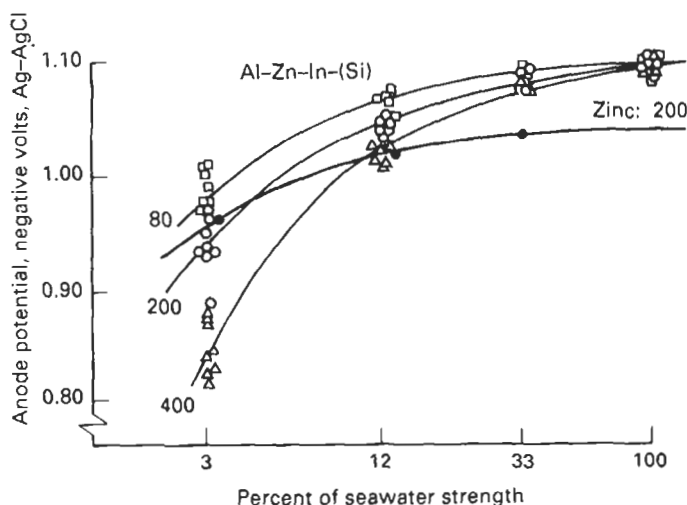


Fig. 10.15 Anode operating potential in semi-saline water exposed for 30–38 days at 15–20°C. Current densities (mA/ft²): 400 (Δ); 200 (○); 80 (□) (after Schreiber and Murray²¹)

The capacity of an anode is dependent on the anode current density²¹. To some extent it will be governed by the exposure environment but, in part, is within the control of the design. Certainly wholly unsuitable current densities can usually be avoided. At lower operating current densities some anodes exhibit reduced capacity; this is shown in Fig. 10.17. Long periods of low operating current density can lead to passivation. This may result in failure to activate when the current demand increases (as can occur with anodes on coated structures when the coating deteriorates).

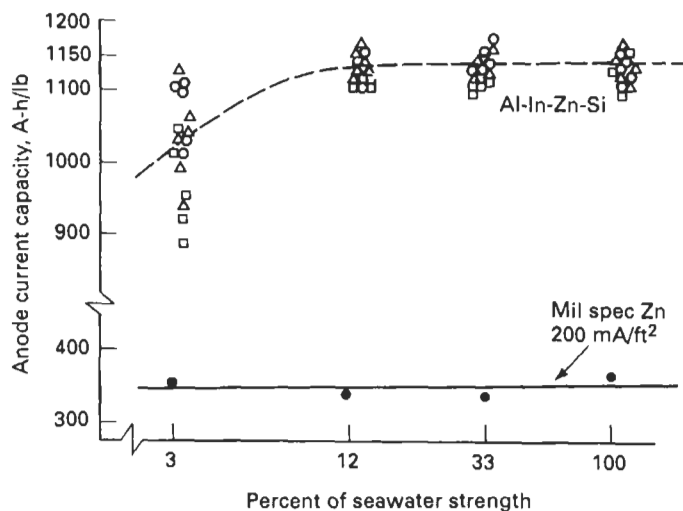


Fig. 10.16 Anode current capacity in semi-saline water exposed for 30–38 days at 15–20°C. Field assembly using diluted seawater. Current densities (mA/ft²): 400 (Δ); 200 (\circ); 80 (\square) (after Schreiber and Murray²¹)

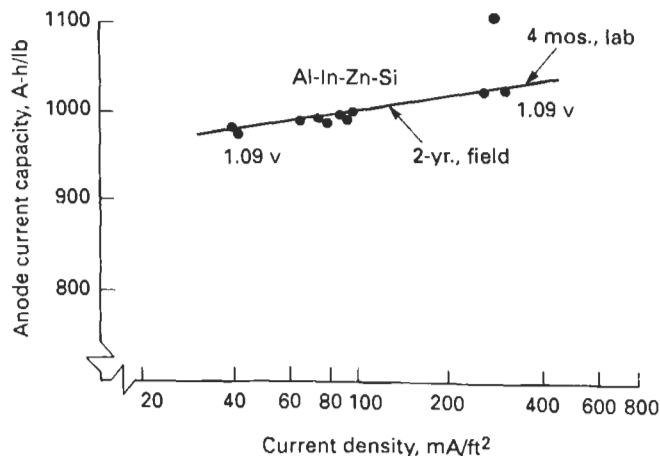


Fig. 10.17 Performance of commercially-cast anodes in field trials (free-running) over wide current density range in ambient Gulf of Mexico mud. Potentials: negative volts versus Ag/AgCl. Zn: 310–350 Ah/lb at 40 and 80 mA/ft² (after Schreiber and Murray²¹)

Selecting the Appropriate Anode Material

It is desirable to choose an anode material with the lowest cost per ampere hour of current supplied. However, the choice is often governed by other constraints and becomes a compromise.

Zinc

Of all the anode materials, zinc is arguably the most reliable. It has, with few exceptions, reliable electrochemical performance. These exceptions lie within the area of high temperature operation. Zinc provides the lowest driving voltage of the generic alloy types. It is therefore unsuitable in highly resistive soils, as Fig. 10.18 shows, and low salinity waters. However, an operating potential of -1.05 V vs. Ag/AgCl/seawater cannot lead to over-protection which is an advantage where concerns for coating disbondment and hydrogen damage of high strength steel (>700 MPa¹³) exist.

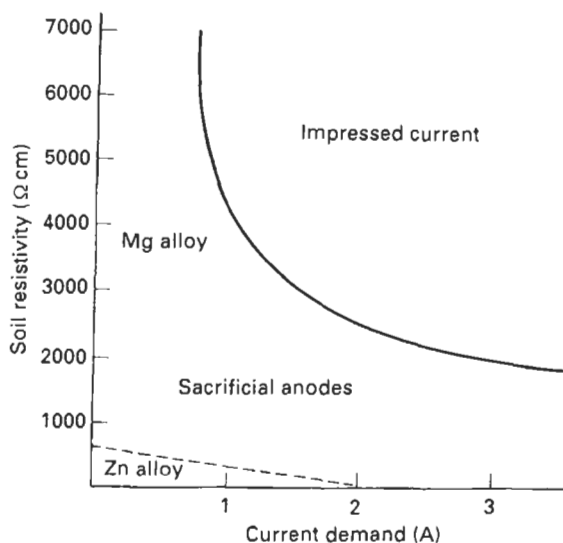


Fig. 10.18 The effect of soil resistivity and current demand on the choice between impressed-current and sacrificial anode protection (after Ashworth *et al.*²⁵)

Zinc anodes have a poor capacity (780 Ah/kg) compared with aluminium (>2500 Ah/kg). However, zinc is not susceptible to passivation in low chloride environments or as a consequence of periods of low operating current density. The reliable operational characteristics of zinc often outweigh the apparent economic attraction of aluminium which can passivate under such conditions.

Zinc anodes do not find application at temperatures in excess of 50°C . Zn-Al-Cd alloys suffer intergranular decohesion, and high purity zinc will passivate. Zinc anodes are not predominant in onshore or offshore applications, but they find considerable use under both conditions.

Aluminium

The great attraction of aluminium anodes is their very high capacity, over three times that of zinc. They are attractive from a cost point of view and

also offer substantial weight savings which can be of great importance (e.g. offshore structures).

Aluminium anodes comprise essentially three generic types: Al-Zn-In, Al-Zn-Hg and Al-Zn-Sn. Since Al-Zn-Sn alloys have largely been superseded, they will not be discussed further. Indium and mercury are added to aluminium to act as activators, i.e. to overcome the natural passivation of aluminium. Despite this, aluminium anodes are not suitable for low chloride environments which would lead to passivation. These anodes are therefore not used for land-based applications (although examples of use in environments such as swamps do exist). Similarly their use in low chloride aqueous environments such as estuaries must be viewed with caution.

The choice between Al-Zn-In and Al-Zn-Hg may well be influenced by their respective operating potentials and capacities. Where an additional driving voltage is required (such as in seabed mud), Al-Zn-In anodes may be preferred to ensure adequate structure polarisation. Alternatively, a lower driving potential may be acceptable where the additional capacity (and hence weight saving) is the predominant factor; this favours Al-Zn-Hg anodes.

Aluminium anodes are less constant in their electrochemical characteristics than zinc. This presents no major problem provided the designer is aware of their properties. They suffer from reduced capacity and increased operating potential (and hence risk of passivation) with increasing temperatures above approximately 50°C (Fig. 10.14), decreasing salinity (Figs. 10.15 and 10.16) and decreasing operating current density (Fig. 10.17).

Aluminium alloys are susceptible to thermite sparking when dropped on to rusty surfaces. Consequently their use may be subject to restrictions. For example, in ships' tanks the weight of the anode and the height that it is suspended are strictly controlled. This is because thermite sparking is dependent on the kinetic energy of the anode.

Aluminium alloy anodes based on Zn-Al-In and Zn-Al-Hg have now become the work-horse materials for seawater service.

Magnesium

Magnesium anodes are of two generic types, Mg-Mn and Mg-Al-Zn. Both alloy systems have a high driving voltage and therefore find application in high resistivity environments; soils and fresh, or brackish, waters for example. The Mg-Mn alloy is useful in particularly resistive environments (up to 6 000 ohm cm) as a result of an available driving voltage 200 mV greater than Mg-Al-Zn anode. Because magnesium is non-toxic its use is permissible in potable water systems where the conductivity is low.

The high driving voltage may, however, result in overprotection. Combined with relatively poor capacity (1 230 Ah/kg) and high unit cost these disadvantages mean that magnesium rarely finds application in subsea environments where alternatives are available. Despite this, Mg-Al-Zn anodes have been used in seabed mud and for rapid polarisation of structures (in ribbon form).

The susceptibility of magnesium to thermite sparking when dropped onto rusty surfaces can preclude its consideration for applications involving a spark hazard, e.g. tankers carrying inflammable petroleum products.

Magnesium is the predominant sacrificial anode material for onshore use.

Anode Testing

Tests of sacrificial anode materials are generally conducted for three reasons: for screening (or ranking), performance information and quality control.

The application of sacrificial anodes for the protection of structures requires the development of suitable anode materials for the exposure environment. Screening tests enable the rapid selection of materials which show potential as candidates for the given application. These tests may typically use a single parameter (e.g. operating potential at a defined constant current density) as a pass/fail criterion and are normally of short duration (usually hours) with test specimen weights of the order of hundreds of grams. The tests are not intended to simulate field conditions precisely.

Performance testing is long term (months to years). Once a potentially attractive formulation has been determined it is used to produce detailed data on its performance and behaviour as an anode material under the anticipated exposure conditions. For this reason the test should mirror as closely as possible the expected operating conditions, or where practicable be conducted in the field. Large specimens (tens or hundreds of kilograms) may be used for these tests.

Quality control tests are intended to detect produced materials which deviate from manufacturing specifications, and thus may result in questionable performance. The materials are usually subjected to spectrographic analysis which is the primary quality control check. The exposure tests are necessarily of short duration (hours or days), in which the test conditions attempt to reflect the environment of operation, for example using artificial seawater for a marine application. Since a property that is reproducible and indicative of a consistent quality anode is all that is required, there is no attempt to mirror, except in the crudest fashion, current density profiles.

Test methods available are the free-running test (galvanic cell), galvanostatic test (constant current) and potentiostatic test (constant potential). These are always run in conjunction with visual examinations with particular emphasis on dissolution pattern.

The critical information required from testing may include one or all of the following: tendency to passivation, anode operating potential and capacity. The tests, whilst all capable of producing information on the above, tend to be particularly suited to certain applications. For example potentiostatic testing is useful for evaluating passivation tendencies but not generally appropriate to anode capacity determination.

Cathodic Protection System Design

Design Parameters

Before a satisfactory cathodic protection system using sacrificial anodes can be designed, the following information has to be available or decided upon:

1. the area of the steelwork to be protected;
2. the type of coating, if any, that is to be used;
3. the cathodic current density;
4. cathodic protection system life.

Area of Steel Requiring Protection and Coating Considerations The area of bare steel to be protected is usually calculated from drawings and knowledge of the actual structure and must account for all electrically continuous steelwork exposed to the electrolyte. Steelwork not specified in drawings and subsequently overlooked is a common cause of underdesign. In practice the area is usually taken assuming the steel surfaces to be flat without corrugations, indentations or surface roughness. An allowance for uncertainties in real area is normally involved.

Many structures are coated. Thus the presented area far exceeds the area of steel to be protected, which is restricted to uncoated areas and holidays in the coating. It is therefore practice to assume an arbitrary level of coating breakdown for coated areas to obtain the area of metal requiring cathodic protection:

$$\text{Area} = \frac{\text{presented area} \times \% \text{ breakdown}}{100}$$

Of course the breakdown will vary through the life of a structure with the result that the area requiring protection will change. Various estimates of coating breakdown have been made and Table 10.12 provides one such. It will be seen that Table 10.12 assumes a rate of breakdown that varies with time. The significance of the area of steelwork is that the greater the area the greater the weight and/or area of anode material required for protection.

Table 10.12 Guide to coating breakdown for offshore structures¹³

Lifetime (years)	Coating breakdown (%)		
	Initial	Mean	Final
10	2	7	10
20	2	15	30
30	2	25	60
40	2	40	90

Cathodic Current Densities for Protecting Steel Examples of current density requirements for the protection of steel (to achieve a steel potential of -0.8 V vs. Ag/AgCl/seawater) are given in Tables 10.13 and 10.14. It should be realised that the current demand of a structure will be influenced by, *inter alia*, temperature, degree of aeration, flow rate, protective scales, burial status, presence of bacteria and salinity.

It is important that the correct current density requirement is assigned for design purposes. If too high a value is used the structure may be wastefully overprotected, whereas a value too small will mean that the protection system will underprotect and not achieve its design life.

Table 10.13 Current density used in ship hull cathodic protection design

Typical Coatings	Self Polishing	Coal Tar Epoxy	Aluminium Bitumen	Conventional		
New Hulls						
Deep Water to Deep Water	0.75	1.5	2	3	5	Design Current Density
Principally Deep Water	1.25	2.5	3	5	6	mA/sq.ft.
Occasional Scour	3	4	5	6	7	Typical Coatings
Ice Damage Frequent Scour	6	6	8	10	10	Retrofits
		Self Polishing	Coal Tar Epoxy	Aluminium Bitumen	Conventional	

Table 10.14 Guidance on minimum design current densities for cathodic protection of bare steel¹³

Area	Current density (mA/m ²)		
	Initial	Mean	Final
North Sea (northern sector, 57–62°N)	180	90	120
North Sea (southern sector, up to 57°N)	150	90	100
Arabian Gulf	130	70	90
India	130	70	90
Australia	130	70	90
Brazil	130	70	90
West Africa	130	70	90
Gulf of Mexico	110	60	80
Indonesia	110	60	80
Pipelines (burial specified)	50	40	40
Saline mud (ambient temperature)	25	20	15

System Life Cathodic protection systems may be designed with a life of between 1 and 40 years. The greater the time of protection, the greater the mass of anode material that is required.

Intermittant exposure and local conditions need to be considered also. The ballast or storage tanks of ships will experience periods of complete submergence, partial coverage and may at times be empty. Similarly, the

wetted areas of offshore structures may be governed by tidal and seasonal variations. Local requirements must therefore be considered in order to achieve the optimum life of the system.

Calculating the Weight and Number of Individual Anodes

Firstly, the total weight of anode required to protect the structure for its projected life is calculated. This is given by:

$$W = \frac{i_{av} A l 8760}{C} \quad (10.14)$$

where W = total mass of anode material (kg)
 A = structure area to be protected (m²)
 i_{av} = mean structure current density demand (A/m²)
 l = design life in years (1 year = 8 760 h)
 C = anode capacity (Ah/kg)

Obviously, the total weight of the anode material must equal or be greater than the total weight, W , calculated above. Similarly each anode must be of sufficient size to supply current for the design life of the cathodic protection system. The anodes must also deliver sufficient current to meet the requirements of the structure at the beginning and end of the system life. That is, if current demand increases (as a result of coating breakdown, for example) the output from the anodes should meet the current demands of the structure.

Anode Size and Shape

In practice there is often not an extensive range of suitable anode sizes from which to select. Economics may dictate an 'off-the-shelf' choice from a manufacturer or the anode shape may have to conform with the geometric limitations of the structure. Consequently, the choice of anode size and shape is often limited.

The current output from an anode will depend on its surface area. Generally, larger anodes will have a higher current output. Anodes of the same weight but differing shape, can have different outputs because the surface area to weight ratio will not be equal for all forms. Thus, for a given weight of anode the shape will offer a degree of flexibility when considering current output.

Anode Output

Anode output is the current available from the anode under the design conditions. It will depend on the shape of the anode, the resistivity of the environment, the protection potential of the structure and the anode operating potential. It is defined as:

$$I = \frac{[E_2 - E_1]}{R} \quad (10.15)$$

where I = anode output (A)
 E_1 = operating potential of the anode (V)
 E_2 = protection potential (V)
 R = anode resistance (ohm)

The protection potential of steel in aerobic environments is taken as -0.80 V (vs. Ag/AgCl/seawater).

Anode Resistance

Table 10.15 lists those formulae suitable for the calculation of anode resistance, R , under submerged conditions. Similar formulae exist for buried conditions²⁶.

Table 10.15 Resistance formulae for submerged anodes¹³ of various geometries

Anode type	Resistance formula
Slender anodes mounted at least 30 cm offset from platform member.	$R_a = \frac{\rho}{2 \cdot \pi \cdot L} \left \ln \frac{4 \cdot L}{r} - 1 \right $ <p> ρ = resistivity L = length of anode r = radius of anode (for other than cylindrical shapes, $r = C/2\pi$, where C = cross section periphery). </p>
Slender anodes mounted at least 30 cm offset from platform member. $L < 4r$	$R_a = \frac{\rho}{2 \cdot \pi \cdot L} \left\{ \ln \left \frac{2 \cdot L}{r} \left(1 + \sqrt{1 + \left(\frac{r}{2 \cdot L} \right)^2} \right) \right + \frac{r}{2 \cdot L} - \sqrt{1 + \left(\frac{r}{2 \cdot L} \right)^2} \right\}$
Flat plate anodes	$R_a = \frac{\rho}{2 \cdot S}$ <p>S = arithmetic mean of anode length and width</p>
Other shapes and bracelet anodes	$R_a = \frac{0.315 \cdot \rho}{\sqrt{A}}$ <p>A = exposed surface area of anode</p>

To calculate the anode resistance a knowledge of the environmental resistivity is required. For submerged anodes the water resistivity can be obtained from graphical representations such as Fig. 10.19, provided that the temperature and water density are known. However, field data are preferable and, in the case of soils that have widely varying resistivities, they are essential.

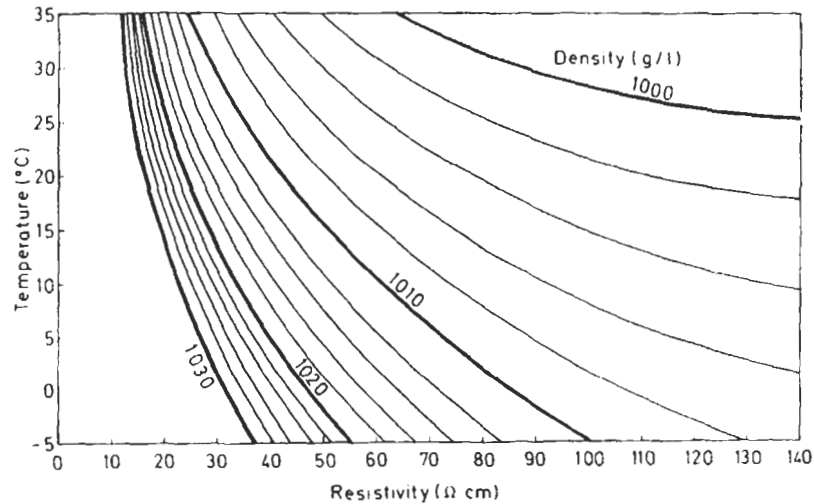


Fig. 10.19 Water resistivity

Anode Life

Having calculated the resistance, and hence current output the anode life, L , is checked by calculation:

$$L = \frac{MU}{IE} \quad (10.16)$$

where L = effective life of anode (years)

M = mass of single anode (kg)

U = utilisation factor, e.g. 0.75–0.80 for bracelet anodes

E = consumption rate of the anode (kg/Ay) (inverse of capacity in suitable units)

I = anode output (A)

U is purely a function of anode geometry and is the fraction of anode material consumed when the remaining anode material cannot deliver the current required¹³.

Excessive anode life is of no benefit. If the calculated life is unsuitable a different anode size and/or shape should be considered. However, this may not always be possible especially for short-life, coated structures, when dimensional constraints on the anodes may be imposed.

Number of Anodes

The total number of anodes, N , is calculated from:

$$N = \frac{A i_{av}}{I} \quad (10.17)$$

This calculation should yield a practicable number of anodes, i.e. 10 or 10 000 anodes are both clearly unacceptable for the protection of an offshore oil production platform. $N \times M$ must be equal to, or greater than, the total weight of anode material, W , required.

It is difficult to achieve both the exact current output and precise weight of anode material simultaneously. Consequently a compromise is reached, but both must at least match design requirements.

A check to ensure that the anodes will deliver sufficient current to protect the structure at the end of the design life should be conducted. This entails calculating the expected anode output at the end of its life and checking that it meets the demands of the structure. Generally the output is calculated using a modified resistance based on an anode that is 90% consumed.

Anode (and current) Distribution

It is evident that a greater number of anodes distributed over the structure will improve current distribution. However, aside from the unacceptable cost incurred by attaching excessive numbers of anodes, an anode must continue to function throughout the life of the structure and must, therefore, be of sufficient size to meet the design life. A very large number of heavy anodes is clearly impracticable and uneconomic.

It is essential to ensure adequate current distribution such that all of the exposed structure remains protected; particularly important, for example, for the nodes of an offshore steel structure. Similarly, over-protection should be avoided. Thus, sacrificial anodes need to be distributed to ensure that the protection potential over the whole structure is achieved.

A degree of flexibility in output to weight ratio from anodes can be achieved by varying the anode shape (as discussed above). This may, for example, provide a greater number of anodes with reduced output, whilst maintaining the desired anode life. Hence improved current distribution can be achieved.

The proximity of the anodes to structures is also important. For example, if the sacrificial anodes are placed on, or very close to, steel pipework in soil then the output from the face of the anodes next to the steelwork can be severely limited. Alternatively, in high conductivity environments, corrosion products may build up and wedge between the anode and the structure. The resulting stresses can lead to mechanical failure of the anode. On the other hand, when anodes are located at an appreciable distance from the steelwork, part of the potential difference will be consumed in overcoming the environmental resistance between the anode and cathode.

Complex computer models are now available to assist in defining the optimum anode distribution²⁷.

The Anode Insert

The anode insert must be strong enough to support the weight of the anode and must be capable of being welded, or mechanically fixed to the cathode.

It should be appreciated that the attachment may be required to withstand the launching and pile driving of a steel jacket for offshore applications.

Consideration must be given to the ease and speed of anode fixing, as this is a significant part of the total installation cost. The methods of fixing anodes to flat, vertical or horizontal surfaces are relatively well known and simple. The methods of fixing anodes to curved surfaces of pipelines and immersed structures are more complex, and generally require more steel insert. Figure 10.20 shows some methods of attaching anodes to curved surfaces. Figure 10.20e shows a pipeline coated with concrete with the anodes attached and with the anode thickness the same as that of the concrete. In practice, the coating would be brought up to the edge of the anode and cover the whole of the steel pipework.

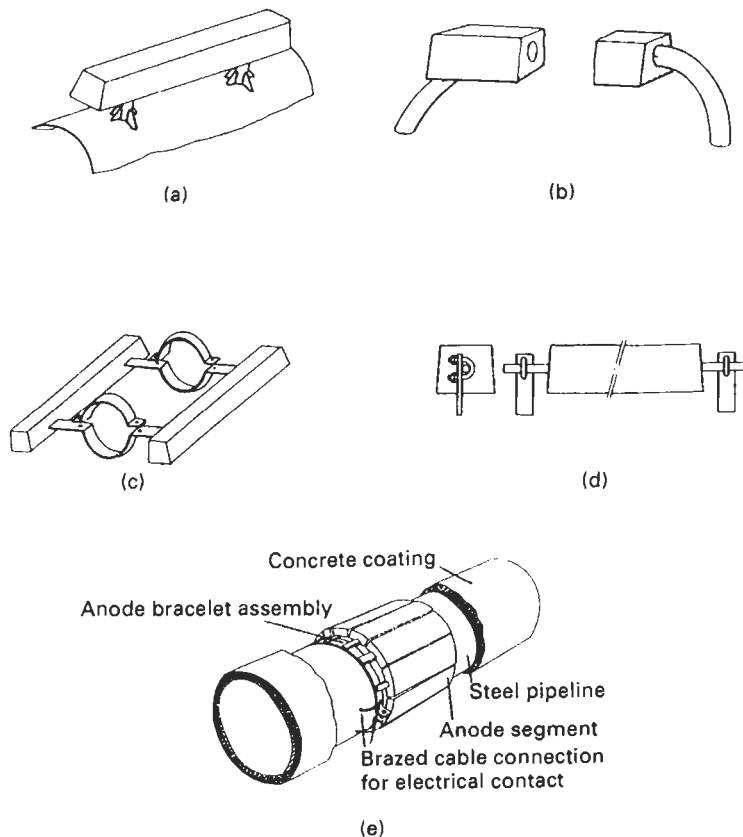


Fig. 10.20 Typical anode shapes and fixing methods. (a) Offshore stand-off anode; (b) Stand-off anode - types of bowed core; (c) Stand-off anode, clamp fixings; (d) Typical tank fixing for shipping; (e) Bracelet anode assembly

Backfills for Anodes

When zinc or magnesium anodes are used for cathodic protection onshore²⁸⁻³⁰, they are usually surrounded by a backfill, which decreases the electrical resistance of the anode. Small anodes are usually surrounded with backfill in bags and large anodes are usually surrounded with a loose backfill during installation. The backfill prevents the anode coming into contact with the soil and suffering local corrosion thus reducing the capacity. By surrounding the anodes with a backfill, the combination of the anode with soil salts is reduced and this helps prevent the formation of passive films on the anode surface.

The effect of the backfill is to lower the circuit resistance and thus reduce potential loss due to the environment. The additive resistances of the anode/backfill and backfill/soil are lower than the single anode/soil resistance. Backfills attract soil moisture and reduce the resistivity in the area immediately round the anode. Dry backfill expands on wetting, and the package expands to fill the hole in the soil and eliminate voids.

For use in high resistivity soils, the most common mixture is 75% gypsum, 20% bentonite and 5% sodium sulphate. This has a resistivity of approximately 50 ohm cm when saturated with moisture. It is important to realise that carbonaceous backfills are relevant to impressed current anode systems and must not be used with sacrificial anodes. A carbonaceous backfill is an electronic conductor and noble to both sacrificial anodes and steel. A galvanic cell would therefore be created causing enhanced dissolution of the anode, and eventually corrosion of the structure.

Other Considerations

Calcareous Scale

A consequence of cathodic protection in seawater is the formation of a protective calcareous scale³¹. The increased local pH at the steel surface caused by hydroxyl production (a product of the cathodic reaction) favours the deposition of a mixed scale of CaCO_3 and Mg(OH)_2 . This scale is beneficial since it is protective and non-conducting, thus reducing the cathodic current density. Ensuring a high current density in the early period of operation will encourage calcareous scale deposition and thus reduce the current requirements in the long term (see Section 10.1 'Principles of Cathodic Protection').

The build-up of calcareous deposits is a complex topic. Very high current densities will not necessarily result in the most protective scale. In the extreme, hydrogen evolution may rupture the scale resulting in reduced protection. An optimum current density will exist, and this should be recognised.

Combined Alloy Anodes for Rapid Structure Polarisation

New combined (or binary) alloy sacrificial anodes have been developed³². An aluminium anode, for example, might have attached to it a short-life supplementary magnesium anode, or anodes, for quick polarisation of the structure. The overall reduction in structure current requirements is claimed to result in an anode weight saving of 35–50%³².

Flame Sprayed Aluminium

The use of flame sprayed aluminium (FSA) with a silicon sealer paint has been applied to protect high-strength steel tension legs of a North Sea production facility³³. The FSA system primarily acts as a very effective barrier coating. In addition the coating has significant anodic capability and aluminium corrosion products serve to plug coating defects. The sealer, although reducing the anodic current output, serves to increase the service life of the FSA coating. This coating system is subject to strict control of application procedures.

Protection of High-Alloy Steels

High-alloy pipeline steels (e.g. austenitic–ferritic or duplex) have been used where the product stream demands materials with better corrosion resistance than carbon steel. In practice the external corrosion resistance of these materials cannot be guaranteed, so cathodic protection is employed to protect areas which may be subject to corrosion.

Concern about hydrogen damage has led to much debate regarding limits for protection potentials of high-alloy steels. However, it is thought that under normal seawater service and cathodic protection conditions, these materials will not be adversely affected provided that the microstructure has at least 40% austenite present³⁴. This latter point is of particular importance to welds and their heat affected zone where careful control of heat input is necessary to maintain a favourable microstructure.

The latter part of this chapter has dealt with the design considerations for a sacrificial anode cathodic protection system. It has outlined the important parameters and how each contributes to the overall design. This is only an introduction and guide to the basic principles cathodic protection design using sacrificial anodes and should be viewed as such. In practice the design of these systems can be complex and can require experienced personnel.

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10.3 Impressed-current Anodes

Impressed-current Anodes for the Application of Cathodic Protection

Numerous materials fall into the category of electronic conductors and hence may be utilised as impressed-current anode material. That only a small number of these materials have a practical application is a function of their cost per unit of energy emitted and their electrochemical inertness and mechanical durability. These major factors are interrelated and—as with any field of practical engineering—the choice of a particular material can only be related to total cost. Within this cost must be considered the initial cost of the cathodic protection system and maintenance, operation and refurbishment costs during the required life of both the structure to be protected and the cathodic protection system.

There are obviously situations which demand considerable over-design of a cathodic protection system, in particular where regular and efficient maintenance of anodes is not practical, or where temporary failure of the system could cause costly damage to plant or product. Furthermore, contamination of potable waters by chromium-containing or lead-based alloy anodes must lead to the choice of the more expensive, but more inert, precious metal-coated anodes. The choice of material is then not unusual in being one of economics coupled with practicability.

Although it is not possible in all cases to be specific regarding the choice of anode material, it is possible to make a choice based upon the comparative data which are at present available. Necessary factors of safety would be added to ensure suitability where lack of long-time experience or quantitative data necessitate extrapolation or even interpolation of an indefinite nature.

The manufacture, processing and application of a particular material as an impressed-current anode requires knowledge of several physical characteristics. Knowledge and attention to these characteristics is necessary to design for anode longevity with maximum freedom from electrical and mechanical defects.

The various types of materials used as anodes in impressed-current systems may be classified as follows:

1. *Precious metals and oxides*: platinised titanium, platinised niobium, platinised tantalum, platinised silver, solid platinum metals, mixed metal oxide-coated titanium, titanium oxide-based ceramics.
2. *Ferrous materials*: steel, cast iron, iron, stainless steel, high-silicon iron, high-silicon molybdenum iron, high-silicon chromium iron, magnetite, ferrite.
3. *Lead materials*: lead-antimony-silver, lead with platinum alloy micro-electrodes, lead/magnetite, lead dioxide/titanium, lead dioxide/graphite.
4. *Carbonaceous materials*: graphite, carbon, graphite chips, coke breeze, conductive polymer, conductive paint.
5. *Consumable non-ferrous metals*: aluminium, zinc.

Combination Anodes

These are anodes that, to reduce costs, use a combination of materials, sometimes coaxially, to extend the life of the primary anode, reduce resistance to earth, improve current distribution, facilitate installation and improve mechanical properties. Often the so-called 'anode' is primarily a means of conducting the current to the more rapidly consumable anode material. These can be classified as follows:

1. *Canister anodes*: consist of a spirally wound galvanised steel outer casing containing a carbonaceous based extender which surrounds the primary anode element which may be graphite, silicon iron, magnetite, platinised titanium, mixed metal oxide-coated titanium or platinised niobium, etc.
2. *Groundbeds*: consist of a carbonaceous extender generally coke breeze and graphite, silicon-iron scrap steel, platinised titanium or niobium anodes.
3. *Co-axial anodes*: These are copper-cored anodes of lead silver, platinised titanium and platinised niobium.

For long lengths of anode it is sometimes necessary to extrude one material over another to improve a particular characteristic. Thus titanium may be extruded over a copper rod to improve the longitudinal conductivity and current attenuation characteristics of the former; lead alloys may be treated similarly¹ to compensate for their poor mechanical properties. It should be noted that these anodes have the disadvantage that, should the core metal be exposed to the electrolyte by damage to the surrounding metal, rapid corrosion of the former will occur.

In flowing water environments a tubular rather than a solid rod cantilever anode may be used to give improved resistance to fatigue failure, since the anode design may result in fatigue failure by vortex shedding at high water velocities.

Failures of impressed-current systems may occur not because of anode failure in a specific environment but because of poor integrity of the anode/cable connection or the use of an inferior cable insulation. Particular

attention must therefore be paid to these aspects of anode construction or rapid failure could take place.

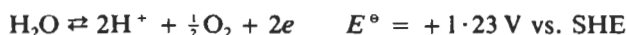
Platinum and Platinum-coated Anodes

The properties of platinum as an inert electrode in a variety of electrolytic processes are well known, and in cathodic protection it is utilised as a thin coating on a suitable substrate. In this way a small mass of Pt can provide a very large surface area and thus anodes of this type can be operated at high current densities in certain electrolyte solutions, such as seawater, and can be economical to use.

When platinum is made the anode in an aqueous solution, a protective electron-conducting oxide film is formed by the following reaction:



Once the protective oxide film is formed current flow may then only occur by oxygen evolution, which in pure aqueous solutions may be represented as



This anode half reaction is highly irreversible and is accompanied by an appreciable overvoltage¹⁰; usually the potential of oxygen evolution is about 0.5 to 0.7 V higher than E° .

In chloride-containing solutions evolution of chlorine will also occur and is usually the predominant anodic reaction even at low Cl^- concentrations, e.g. brackish waters:



The relative proportions of oxygen and chlorine evolved will be dependent upon the chloride concentration, solution pH, overpotential, degree of agitation and nature of the electrode surface, with only a fraction of the current being used to maintain the passive platinum oxide film². This will result in a very low platinum consumption rate.

Tests carried out in the USA and initiated in 1953³ indicate the following consumption rates of precious metals and their alloys: Pt, Pt-12Pd, Pt-5Ru, Pt-10Ru, Pt-5Rh, Pt-10Rh, Pt-5Ir and Pt-10Ir, 6-7 $\text{mg A}^{-1}\text{y}^{-1}$; Pt-20Pd, Pt-50Pd, Pt-20Rh and Pt-25Ir, slight increase in rate; Pt-50Pd, greater increase in rate although the cost of Pd may offset this; Pd, Ag, Pd-40Ag, Pd-10Ru and Pd-10Rh, excessively high rates. The tests were carried out for periods of some months in seawater at current densities ranging from 540 to 5 400 Am^{-2} , and the results appeared to be independent of current density and duration of test.

The dissolution rate of solid rods of high purity platinum over the current density range 1 180 to 4 600 Am^{-2} has also been investigated. Values of 17.5 to 26.3 $\text{mg A}^{-1}\text{year}^{-1}$ were reported over the first year, but the rate decreased to a limiting value of 2.6 to 4.4 $\text{mg A}^{-1}\text{y}^{-1}$ over a 5-year period⁴. The high initial rate was attributed to preferential dissolution at grain boundaries and other high free energy sites. Tests carried out in the

UK^{5,15} on electrodeposited platinum on a titanium substrate indicate a consumption rate in seawater of $8.8 \text{ mg A}^{-1} \text{ y}^{-1}$, although values of up to $15 \text{ mg A}^{-1} \text{ y}^{-1}$ have been quoted elsewhere⁶.

Platinised Titanium

Titanium, which was in commercial production in 1950⁷, is thermodynamically a very reactive metal (machining swarf can be ignited in a similar fashion to that of magnesium ribbon) but this is offset by its strong tendency to passivate i.e. to form a highly stable protective oxide film.

It is a valve metal and when made anodic in a chloride-containing solution it forms an anodic oxide film of TiO_2 (rutile form), that thickens with an increase in voltage up to 8–12 V, when localised film breakdown occurs with subsequent pitting. The TiO_2 film has a high electrical resistivity, and this coupled with the fact that breakdown can occur at the e.m.f.'s produced by the transformer rectifiers used in cathodic protection makes it unsuitable for use as an anode material. Nevertheless, it forms a most valuable substrate for platinum, which may be applied to titanium in the form of a thin coating. The composite anode is characterised by the fact that the titanium exposed at discontinuities is protected by the anodically formed dielectric TiO_2 film. Platinised titanium therefore provides an economical method of utilising the inertness and electronic conductivity of platinum on a relatively inexpensive, yet inert substrate.

Titanium can be forged, bent, cut, stamped, rolled, extruded and successfully welded under argon, making possible a large variety of electrode shapes, i.e. rod, sheet, tube, wire or mesh. It is a very light yet strong material with a high resistance to abrasion.

Cotton^{8,9} was the first to publish results on platinised titanium as an anode material, and the first commercial installation utilising platinised titanium anodes was completed in 1958 at Thameshaven for the protection of a Thames-side jetty.

Manufacture of Platinised Titanium Anodes Platinised titanium anodes are mainly produced by the electrodeposition of a thin coating of Pt from aqueous solutions¹⁰ on to preroughened titanium. Warne¹¹ states that electrodepositing coatings from aqueous plating solutions has the advantage that control of thickness is easily achieved, irregularly shaped substrates can be plated, and the electrodeposited coatings are hard and abrasion resistant, by virtue of the interstitial hydrogen co-deposited in the plating process.

Titanium is a very difficult metal to electroplate because of the presence of an oxide film. Sophisticated pretreatments with acids to remove the oxide film are necessary to achieve good adhesion. Improvements in the level of adhesion can, however, be obtained by heat treatment of the resultant Pt/Ti composites¹².

Electrodeposits of Pt can only be applied as relatively thin coatings that are porous. Although the porosity decreases with increase in deposit thickness, so does the internal stress and if the platinum adhesion is poor the coating may exfoliate. As a consequence, thicknesses of 2.5 to 7.5 μm Pt

are normally used, although it is possible to apply coatings of $12.5 \mu\text{m}$ in one operation and still achieve good adhesion². However, $7.5 \mu\text{m}$ is generally considered the maximum thickness from one plating operation. Thicker deposits may be obtained by deposition in a number of stages, with inter-stage anneals.

Pt electrodeposits may also be produced from molten salt electrolytes. Such a high-temperature process has the advantage that the deposits are diffusion bonded to the titanium substrate and thus have good adhesion, and, if necessary, thick deposits can be produced. However, they have the disadvantage that because of the complexity of the process there is a limitation on the size and shape of the object to be plated, and the resultant deposits are softer and less wear resistant than those from aqueous solutions¹³.

Metallurgically bonded coatings may also be produced. These have the advantage that thick, low porosity, ductile platinum coatings can be produced. These are achieved by electrodeposition of platinum or, more often, by wrapping a thin platinum sheet over a cylindrical billet of titanium, vacuum encapsulating within a copper can, and then extruding it into the required shape¹⁰. The copper sheath, which is used as a lubricant, has the advantage that it prevents fouling of the anode prior to energising.

Platinum coatings may also be thermally sprayed or sputtered onto the titanium, to provide uniform well-bonded coatings. Titanium rod may also be spiral wound with platinum wire¹⁴. However, the use of these techniques is limited.

The Operational Characteristics of Platinised-Titanium Anodes Platinised-titanium anodes have the disadvantage that the protective passive film formed when titanium is made anodic in certain solutions can breakdown. This could result in rapid pitting of the titanium substrate, leading ultimately to anode failure. The potential at which breakdown of titanium occurs is dependent upon the solution composition, as is evident from Table 10.16.

Table 10.16 Breakdown potentials of commercially pure titanium in various environments

<i>Reference</i>	<i>Electrolyte and conditions</i>	<i>Breakdown potential of commercially pure titanium (V)</i>
15	Tests in pure seawater at ambient temperatures	8.5-15
15	Tests in NaCl from 5 g/l to saturated below 60°C	8.5-15
16	Seawater	9-14
17,18	Sulphuric acid	80-100
19	Chloride	8
19	Sulphate	60
19	Carbonate	60
19	Phosphate	60
18	Fluoride	50
18	Bromide	2-3
18	Iodide	2-3
18	Sulphate	>80
18	Phosphate	>80
20	Ratio of sulphate plus carbonate to chloride ions, 4:1	>35
21	River water	50
22	Tap water	80

In seawater the breakdown potential of titanium is often considered to be ~ 9.5 V vs. SHE⁵, whilst values as low as 6 V in 5.8% NaCl solutions have been reported²³. The value of the breakdown potential for titanium is dependent upon the Cl^- concentration and in high purity waters may be relatively high²²; in the case of seawater certain, anions present, for example SO_4^{2-} , favour passivation. It is also dependent upon the level of purity of the titanium and generally decreases with the addition of certain alloying elements. The presence of bromides and iodides will significantly reduce the pitting potential for titanium whilst other ions, notably fluorides and sulphates will tend to increase it. Temperature also has a significant effect on the anodic breakdown voltage of titanium, with an increase in temperature decreasing the breakdown potential.

Platinised titanium anodes may be operated at current densities as high as 5400 Am^{-2} , however at these current densities there is the possibility that the breakdown potential of titanium may be exceeded. The normal operating current density range in seawater is $250\text{--}750 \text{ Am}^{-2}$, whilst that in brackish waters is given as $100\text{--}300 \text{ Am}^{-2}$ ²⁴ with values within the range $100\text{--}150 \text{ Am}^{-2}$ being favoured¹⁰.

The consumption rate for platinised titanium anodes in seawater over the current density range 300 to 5000 Am^{-2} has been found to be directly related to the charge passed, with values of 8.7 to $17.4 \text{ mg A}^{-1} \text{ y}^{-1}$ being generally used as the basis for system design. The consumption rate is also dependent upon solution composition, the rate increasing with decreasing chloride concentration and may reach a peak value of $435 \text{ mg A}^{-1} \text{ y}^{-1}$ at a salt concentration of 2.5 g l^{-1} ¹⁰. The reason for the increased corrosion rates is thought to be associated with the concurrent evolution of oxygen and chlorine, the rates of which are about equal in a neutral solution containing 2.5 g l^{-1} NaCl⁵. In brackish waters the platinum consumption rate may be as high as $174 \text{ mg A}^{-1} \text{ y}^{-1}$, i.e. more than ten times the rate in seawater, and increases with increase in current density²⁴. Notwithstanding this, values of approximately $45 \text{ mg A}^{-1} \text{ y}^{-1}$ have often been used as the basis for design calculations in brackish waters. Baboian²⁵ reports consumption rates of approximately $13 \text{ mg A}^{-1} \text{ y}^{-1}$ in seawater over the current density range 11.8 to 185 Am^{-1} , whilst those in 350 ohm cm water (brackish river water) he reports as $92.3 \text{ mg A}^{-1} \text{ y}^{-1}$ at 11.8 Am^{-2} , increasing to $117.8 \text{ mg A}^{-1} \text{ y}^{-1}$ at 185 Am^{-2} .

The effect of temperature on the consumption rate of platinised titanium anodes has not been found to be significant over the ranges normally encountered in cathodic protection installations, although at elevated temperatures of $90\text{--}95^\circ\text{C}$, consumption rates of $570 \text{ mg A}^{-1} \text{ y}^{-1}$ in 0.02% Na_2SO_4 and 12% NaCl solutions have been reported²¹.

Early failures of platinised titanium anodes have been found to occur for reasons other than increased consumption of platinum or attack on the titanium substrate caused by voltages incompatible with a particular electrolyte. The following are examples:

1. Attack on the substrate in low pH conditions, e.g. when covered in mud or marine growth, prior to energising, has been found to be a possible cause of failure^{21,26}. A commercial guarantee requires that the period in which anodes remain unenergised must not be longer than 8

weeks¹⁹. Indeed, if anodes are to be installed for extended periods prior to energising, they can be coated with a copper anti-fouling paint or with a flash of copper electrodeposit⁵. The copper coating will dissolve when the anode is energised and will not affect the anode's subsequent performance or operation.

2. Attack on the substrate by contact with $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ (calcareous scale) can also cause deplatinisation to occur. Anodes located close to the cathode or operating at high current densities can lead to a rapid build up of calcareous deposit, the major constituents of which are $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ ²⁷. The alkaline conditions so generated can lead to rapid dissolution of the platinum. The calcareous deposit can be removed by washing with dilute nitric acid.
3. The formation of deposits on platinised anodes can cause anode degradation^{12,21}. Thus dissolved impurities present in water which are liable to oxidation to insoluble oxides, namely Mn, Fe, Pb and Sn, can have a detrimental effect on anode life. In the case of MnO_2 films it has been stated that MnO_2 may alter the relative proportions of Cl_2 and O_2 produced and thus increase the Pt dissolution rate¹⁰. Fe salts may be incorporated into the TiO_2 oxide film and decrease the breakdown potential²¹ or form thick sludgy deposits. The latter may limit electrolyte access and lead to the development of localised acidity, at concentrations sufficient to attack the underlying substrate¹⁰.
4. The superimposition of a.c. ripple on the d.c. output from a transformer rectifier can under certain circumstances lead to increased platinum consumption rates and has been the subject of considerable research^{21,28-30}. Indeed, when platinised titanium anodes were first used it was recommended that the a.c. component was limited to 5% of the d.c. voltage¹⁰.

The frequency of the superimposed a.c. voltage signal has also been shown to affect the consumption rate of platinum, which increases with decrease in frequency to 50 Hz and less. It was observed that at 100 Hz (the frequency of the a.c. component signal from a full-wave single phase transformer rectifier) and above, the a.c. signal had a negligible effect on consumption rate, provided of course that the a.c. component did not allow the electrode to become negative. In this case, even at 100 Hz a considerable increase in platinum dissolution can occur³¹. This could be the case with a thyristor-controlled transformer rectifier operating at a relatively low current output. At low-frequency a.c. (2 Hz) an increase in platinum dissolution rate of two to three times has been reported, whilst negative current spikes of a few milliseconds duration at this frequency can cause dissolution rates of approximately $190 \text{ mg A}^{-1} \text{ y}^{-1}$. It is therefore recommended that all spurious waveforms on the d.c. supply to platinised anodes be avoided.

5. Organic impurities in the electrolyte have also been quoted as increasing the rate of platinum dissolution when the metal is used as an anode in electroplating²¹. Saccharose was observed to increase the anodic dissolution of platinum by a factor of ten, in a 3% brine solution³³, yet it did not affect the anodic breakdown voltage for titanium. Other organic compounds that may also have an effect are brightening agents

for Ni plating solutions of the naphthalene trisulphonic acid type, detergents or wetting agents.

6. Fatigue failure due to underdesign or changes in plant operation of cantilever anodes in flowing electrolytes can occur as a result of vortex shedding³⁴. However, with proper design and adequate safety factors these failures can be avoided^{21,35}.
7. Attention must be paid to field end effects, particularly on cantilever anodes, e.g. on long anodes that extend away from the cathode surface. Under these circumstances the anode surface close to the cathode may be operating at a considerably higher current density than the mean value, with the exact values dependent upon the system geometry. The life of the platinising in this region would then be reduced in inverse proportion to the current density.

Platinised-titanium installations have now been in use for 30 years for jetties, ships and submarines^{10,35} and for internal protection, particularly of cooling-water systems³⁶. For the protection of heat exchangers an extruded anode of approximately 6 mm in diameter (copper-cored titanium-platinum) has shown a reduction in current requirement (together with improved longitudinal current spread) over cantilever anodes of some 30%³⁷⁻³⁹. This 'continuous' or coaxial anode is usually fitted around the water box periphery a few centimetres away from the tubeplate.

Platinised-titanium anodes may also be used in soils when surrounded by a carbonaceous backfill. Warne and Berkeley⁴¹ have investigated the performance of platinised-titanium anodes in carbonaceous backfills and conclude that the anodes may be successfully operated in this environment at a current density of up to 200 Am^{-2} . This also supplements the findings of Lewis⁴², who states that platinised-titanium anodes may be used in carbonaceous backfill without breakdown of the titanium oxide film. Success with platinised-titanium anodes has been reported with anodes operating at a few tens of Am^{-2} and failures of anodes have often been attributed to operation at high current densities¹⁰.

Furthermore, the restrictions on operating voltage that apply to titanium in a marine environment are not always relevant to titanium in soils free of chloride contamination. Coke breeze is, however, an integral part of the groundbed construction and ensures a lower platinum consumption rate. However, for some borehole groundbeds, platinised niobium is preferred, particularly in the absence of carbonaceous backfill or in situations where the water chemistry within a borehole can be complex and may, in certain circumstances, contain contaminants which favour breakdown of the anodic TiO_2 film on titanium. In particular, the pH of a chloride solution in a confined space will tend to decrease owing to the formation of HOCl and HCl , and this will result in an increase in the corrosion rate of the platinum.

The high cost of platinised materials for use in borehole groundbeds as opposed to conventional silicon-iron anodes may also be offset by the reduction in required borehole diameter, hence lower installation cost, with the relative economics between the different systems dependent upon a combination of both material and installation costs.

Platinised Niobium and Platinised Tantalum

The principle of these anodes is similar to that of platinised titanium since they are all valve metals that form an insulating dielectric film under anodic polarisation.

Platinum electrodeposition on to tantalum had been carried out as early as 1913⁴³ and the use of platinised tantalum as an anode suggested in 1922⁴⁴, whilst platinum electrodeposition on to niobium was first successfully carried out in 1950⁴⁵.

These anodes are considerably more expensive than platinised titanium, especially when expressed in terms of price per unit volume⁴. Indeed, since niobium is cheaper than tantalum the use of the latter has become rare. The extra cost of Nb anodes may be offset in certain application by their superior electrical conductivity and higher breakdown voltages. Table 10.17 gives the comparative breakdown potentials of Ti, Nb and Ta in various solutions under laboratory conditions.

Table 10.17 Comparison of breakdown potential⁴⁶

<i>Solution</i>	Ti	Nb	Ta
Seawater	9	120	120
Sulphate/Carbonate	60	255	280
Phosphate/Borate	80	250	280
Drinking water	37.5	250	280
Bromides	2-3		

There have been instances reported in the literature where the breakdown potential for Nb and Ta in seawater has been found to be lower than the generally accepted value of 120 V, with reported values in extreme instances as low as 20-40 V^{47,48}. This has been attributed to contamination of the niobium surface from machining operations, grit blasting or traces of copper lubricant used in anode manufacture. These traces of impurities, by becoming incorporated in the oxide film, decrease its dielectric properties and thus account for the lower breakdown voltage. Careful control of surface contamination in the manufacture of platinised niobium is therefore essential to minimise the lowering of the breakdown potential of niobium.

Platinised niobium anodes are prepared by electrodepositing platinum onto grit-blasted niobium, metallurgical co-processing (cladding) or by welding platinum or platinum/iridium wire to niobium rod⁴⁸. They are not prepared by thermal deposition because niobium oxidises at 350°C, and good adhesion cannot be obtained. Both materials may be welded under argon, utilising butt or plasma welding techniques.

Platinised niobium and tantalum anodes have found use in applications where their high breakdown voltages and hence higher operational current densities can be utilised, e.g. ship and cooling system anodes, which may be used in estuarine waters and thus require higher driving voltages, offshore structures where high reliability in service is required, domestic water tanks⁴⁹ and deep well groundbeds⁵⁰. Because of their higher breakdown voltages niobium and tantalum anodes can be operated at higher current densities than platinised titanium. Efrid³² found the consumption rate of

platinised niobium in seawater over the range 5 000 to 10 000 Am^{-2} to be similar to that of platinised titanium, i.e. $7.8 \text{ mg A}^{-1} \text{ y}^{-1}$. However, at a current density of 30 000 Am^{-2} he observed an increase in the platinum consumption rate to $15.6 \text{ mg A}^{-1} \text{ y}^{-1}$ and concluded that this was the limiting current density for operating these anodes. Warne and Berkeley⁴¹ report that the maximum current density for these anodes in seawater is 2 000 Am^{-2} , with a working current density of 500 to 1 000 Am^{-2} . The operating current density selected should, however, be commensurate with the desired anode life, platinum coating thickness and platinum consumption rate in a given environment.

In open-hole deep-well groundbeds, platinised niobium anodes have been successfully operated at current density of 215 Am^{-2} ⁵¹ and in the range 100 to 267 Am^{-2} ⁵². Toncre and Hayfield²⁴ have conducted work on the operating parameters of platinised niobium anodes in brackish waters and simulated groundbed environments. In an open-hole groundbed they concluded that operational current densities of 400 Am^{-2} or higher were the most economical, since this leads to a lower consumption rate in sulphate-containing soils. The platinum consumption rate in a deep-well environment may well alter because of variations in the environmental conditions. On extruded platinised niobium anodes a consumption rate of $175 \text{ mg A}^{-1} \text{ y}^{-1}$ was considered for design purposes, whilst that for electroplated platinised niobium was taken as $87.6 \text{ mg A}^{-1} \text{ y}^{-1}$. In a backfilled deep-well groundbed, evidence of dissolution rates comparable with those for an open-hole environment were reported, i.e. $87.6 \text{ mg A}^{-1} \text{ y}^{-1}$ at 200 Am^{-2} . At lower current densities, namely 100 Am^{-2} , it seems likely that the electrochemical processes would be limited to oxidation reactions involving coke alone and no electrochemical wear* on platinised niobium would occur. Indeed, Baboian¹⁶⁵ reports negligible Pt consumption rates in carbonaceous backfill at current densities from 11.8 to 29 Am^{-2} , increasing to 11.9 mg A^{-1} at 57.9 Am^{-2} and $13.5 \text{ mg A}^{-1} \text{ y}^{-1}$ at 185 Am^{-2} . The wear rates at 57.9 and 185 Am^{-2} were comparable to those Baboian observed in seawater.

The relative merits of platinised titanium and niobium in a deep-well environment, in comparison with those of other anode materials, have been given by Stephens⁵³.

Platinised Silver

This material can be used only in seawater or similar chloride-containing electrolytes. This is because the passivation of the silver at discontinuities in the platinum is dependent upon the formation of a film of silver chloride, the low solubility of which, in seawater, inhibits corrosion of the silver. This anode, consisting of Pt-10Pd on Ag, was tried as a substitute for rapidly consumed aluminium, for use as a trailing wire anode for the cathodic protection of ships hulls, and has been operated at current densities as high as 1 900 Am^{-2} . However, the use of trailing anodes has been found inconvenient with regard to ships' manoeuvrability.

* In the case of the platinum metals the term 'wear' is frequently used in place of corrosion attack.

With the advent of hull mounted anodes this material has been replaced by the superior platinised titanium and niobium anodes and is now seldom used.

Mixed Metal Oxide Coated Titanium

The material was originally developed by Beer^{55,56}, and its major application has been in the production of chlorine and chlorates^{57,58}.

It has now gained acceptance as an impressed current anode for cathodic protection and has been in use for this purpose since 1971. The anode consists of a thin film of valve and precious metal oxides baked onto a titanium substrate and when first developed was given the proprietary name 'dimensionally stable anode', sometimes shortened to DSA. Developments on the composition of the oxide film have taken place since Beer's patent, and this type of anode is now marketed under a number of different trade names.

The anodes are produced by applying a paint containing precious metal salts or organic compounds in an organic solvent to the titanium surface and then allowing the solvent to evaporate. The completed assembly is then heated in a controlled atmosphere to a temperature at which the paint decomposes (between 350 and 600°C)⁵⁹ to give the metal. Platinum does not form an oxide under the conditions selected, but other precious metals namely iridium, ruthenium, rhodium and palladium do. A number of paint coatings may be necessary to obtain the required deposit thickness, which is typically 2–12.5 µm, although deposits up to 25 µm thick have been obtained. Deposits thicker than this become brittle and poorly adherent⁶⁰.

At present only titanium substrates are coated in this way because at the temperatures encountered in the anode manufacturing process, niobium would oxidise. Tantalum can be coated with a mixed oxide but this is a relatively expensive process.

The composition of the mixed metal oxide may well vary over wide limits depending on the environment in which the anode will operate, with the precious metal composition of the mixed metal oxide coating adjusted to favour either oxygen or chlorine evolution by varying the relative proportions of iridium and ruthenium. For chlorine production RuO₂-rich coatings are preferred, whilst for oxygen evolution IrO₂-rich coatings are utilised⁶¹.

The mixed metal oxide coatings consist of a platinum group metal (usually ruthenium, although in some cases two or three metals are used) and an oxide of a non-platinum group metal (usually Ti, Sn or Zr)⁵⁹. The precise composition of the coating is generally considered proprietary information and not divulged by the various anode manufacturers. Indeed, recent studies have shown that a proprietary electroactive mixed metal oxide anode coating used for the cathodic protection of steel in concrete contains Ta, Ir, Ti and Ru⁶². The metal oxide coating has a low electrical resistivity of approximately 10⁻⁷ ohm m, and a very low consumption rate. In seawater the consumption rate is 0.5 to 1 mg A⁻¹ y⁻¹, whilst in fresh waters and saline muds the rate is 6 mg A⁻¹ y⁻¹⁶⁰, at current densities of 600 and 100 Am¹², respectively⁶⁰.

In fresh waters, where there is a limited chloride concentration, the predominant reaction is oxygen evolution. This process gives rise to a high level of acidity which may account for the increased oxide consumption rates observed in this environment. The current densities normally used for design purposes are 600 Am^{-2} for seawater, and 100 Am^{-2} for fresh water, saline mud and coke breeze backfill⁶³. Higher current densities may be utilised in certain circumstances but this reduces the anode life for a given coating thickness. The relationship between current density and life for the mixed metal oxide coated electrodes is non-linear and higher current densities increase the consumption rate of the oxide.

The approximate value for the oxide coating dissolution rate in relation to current density⁶³ in soils and fresh water is:

$$\log_{10} L = 3.3 - \log_{10} i$$

and in seawater is:

$$\log_{10} L = 2.3 - 0.4 \log_{10} i$$

where i is the current density (Am^{-2}) and L is the coating life (years). Indeed, with current densities of 4000 Am^{-2} in 3% NaCl rapid consumption rates of RuO_2 coatings have been reported⁶⁵.

The oxide coatings are porous and therefore the limitations on operating voltage for platinised titanium anodes apply as well to the oxide-coated titanium electrodes. It has been reported that breakdown of mixed metal oxide anodes may occur at 50–60 V in low-chloride concentration water but at only 10 V in chloride-rich environments⁶⁰.

These anodes, like platinised Ti may be supplied in different forms e.g. rod, tube, mesh, wire, etc. They may be used for the cathodic protection of offshore structures, heat exchangers, or even pipelines as they can be installed in the soil surrounded by carbonaceous backfill, and are comparable in cost to platinised titanium⁶⁴.

Conductive Titanium Oxide Based Ceramics

An electrically conductive titanium oxide based ceramic material has been developed recently, and is marketed under the trade name 'Ebonex'⁶⁶. This material consists principally of Ti_4O_7 , but may also contain some higher oxides. It is black in colour, has an electrical resistivity of less than $2 \times 10^{-4} \text{ ohm m}$ and can be operated at current densities up to 100 Am^{-2} in 1% NaCl, however, if coated with a precious metal it can be operated at considerably higher current densities up to 400 Am^{-2} ⁶⁷. However, no information is given by the manufacturers on the consumption rate of this particular material other than that it is inert. It is both porous and brittle, although its mechanical strength can be improved and porosity reduced by resin impregnation, preferably with inorganic fillers. It has a high overpotential for oxygen evolution, is not affected by current reversal, has no restriction on operating voltage and the makers claim it has an excellent resistance to both acid and alkali.

To date the material has been used as an electrode in electro-winning, electro-chlorination, batteries and electrostatic precipitators, but only to a very limited extent in cathodic protection.

Ferrous Materials

Steel

One of the earliest materials to be used in power-impressed cathodic protection was steel. Its economy lies in situations where steel scrap is available in suitable quantities and geometry and it is only in such situations where its use would now be considered.

The anode tends to give rise to a high resistance polarisation due to the formation of a voluminous corrosion product, particularly when buried as opposed to immersed. This can be alleviated by closely surrounding the scrap with carbonaceous backfill; this of course increases the cost if the backfill is not also a local by-product. It is necessary under conditions of burial to ensure compactness and homogeneity of backfill (earth or carbon) at all areas on the steel, otherwise particularly rapid loss of metal at the better compacted areas could lead to decimation of the groundbed capacity.

The problem of the high resistance polarisation decreases with increasing water content and salinity, such as prevails during immersion in seawater, where these anodes are particularly useful. Since no problems of burial arise in that environment an endless variety of disused iron-ware has been utilised for anodes, e.g. pipes, piling, machinery, rails and even obsolete shipping which has not been economic to salvage. Consumption rates in excess of the theoretical value have been reported for steel in different waters^{68,69}.

Experimental installations have been established from time to time to demonstrate the possibility of using ferrous metals in anolytes⁷⁰⁻⁷² selected to minimise polarisation and to reduce metal ionisation by making the metal passive.

The use of carbonaceous extender is of value if segregation of a steel anode in soil might be expected to result from high localised corrosion rates. Continuity of the anode is facilitated by the bridging effect of the extender. One example of this is in deep-well groundbeds, installed in stratified soils of widely differing ground resistivities, where a well casing may be filled with coke breeze. Commercial examples of these are known to be working well after periods of 28 years⁷³.

One advantage of steel as an anode is the low gassing at the electrode during operation, since the predominant reaction is the corrosion of iron. Thus, the problem of resistive polarisation due to gas blocking, as may be the case with more inert materials, does not occur. Iron compounds do, of course, form but these do not appreciably affect the anode/soil resistivity. Furthermore, the introduction of metallic ions, by anode corrosion, into the adjacent high resistivity soil is beneficial in lowering the resistivity.

It is necessary to ensure the integrity of anode cable connections and to give consideration to the number of such connections related to longitudinal resistance of the anode and current attenuation, if early failure is to be avoided.

Cast Iron

Cast iron may be used under similar circumstances, but has inferior mechanical properties. It has been used, although not in current practice, for internal cathodic protection, where it has been demonstrated that the presence of ferrous ions in water is of benefit in reducing sulphide-induced attack on Cu alloy tube plate and tubes⁷⁴. Water treatment has now been found to be a more practical method.

Iron

Swedish iron is sometimes used as galvanic wastage plates in heat exchangers, particularly for marine applications. This is possibly based on tradition, since it cannot be the most economical method in the light of current cathodic-protection practice. The material is not currently used as an impressed-current anode.

Stainless Steel

Stainless steel has been tried as an inert anode, mainly under laboratory conditions and with only partial success. Even at low current densities in fresh water the majority of alloys pit rapidly, although others show the ability to remain passive at a low current density^{75,76}. However, at practical current densities, the presence of chloride ions, deposits on the anode or crevice corrosion at the anode support lead to rapid failure⁷⁷, but it may be possible that stainless steel could give useful service under certain conditions and with particular alloys⁷⁸.

High Silicon Iron (HSI)

These are iron alloys that contain 14–18% Si and are reported as first being developed in 1912⁷⁹, although it was not until 1954 that they were first evaluated for use as impressed-current anode material in cathodic protection⁶⁸. Its major disadvantage is that it is a hard brittle material unable to sustain thermal or mechanical shock.

The only practical method of machining is by grinding, and to obviate machining it is cast into fairly standard sizes to suit the general requirements of industry. HSI has a long successful history as a corrosion-resistant material in the chemical industry for such items as acid storage vessels and has been used in this application for more than 60 years. A typical analysis for HSI anodes is 14.5% Si, 0.75% Mn, 0.95% C, remainder Fe. The anodes manufactured in the UK conform to BS 1591:1975 which lists the permissible Si content range as between 14.25 and 15.25%, whilst the maximum content of other elements is given as 1% C, 0.1% S and 0.25% P.

Used anodically it readily forms a protective film which is reformed if removed mechanically. This is grey-white in appearance and has a tendency to flake under the compressive stress produced at thickened areas. The film

is 50% porous and contains 72–78% SiO_2 ⁷⁹. The film, formed in this way, is a fairly good electron conductor, even though SiO_2 in its natural state is a dielectric. The mechanism whereby the SiO_2 becomes a conducting oxide has been reviewed in some detail by Shreir and Hayfield¹⁰, and is probably associated with doping of the SiO_2 with Fe ions.

A coke-breeze backfill can be installed around the anodes buried in soil, so as to reduce the groundbed resistance to earth, anode current density and concentration of oxidising gases around the anode, thus improving the operational life. There is a tendency, when buried as opposed to immersed, for the surface resistance of such an anode to increase, but not to an extent that affects performance. The large resistance changes sometimes reported are usually due to gaseous polarisation (gas blocking) caused by poor venting or inadequate compaction and quantities of backfill.

HSI anodes are subject to severe pitting by halide ions and this precludes their use in seawater or other environments in which these ions may be present in quantity. They are ideal for fresh-water applications (below 200 p.p.m. Cl^-), although not for temperatures above 38°C. The addition of Mo or Cr to the alloy can improve performance under these conditions, with an upper limit of temperature of 56°C⁸⁰, which may be affected by the composition of the water and operating conditions.

The wastage rate of HSI depends upon the current density and the nature of the soil or water in which the anode is used. HSI is superior to graphite in waters of resistivity greater than 10 ohm m, but in waters of 0.5 ohm m and below HSI is susceptible to pitting. From collated experience in fresh water in the pH range 3 to 10 a nominal consumption rate of approximately 0.1 kg $\text{A}^{-1} \text{y}^{-1}$ at 20°C has been observed. This is of course dependent upon solution composition and temperature⁸¹. A number of reports on the performance of HSI anodes in different environments have been produced^{81–84}.

The consumption rate of HSI anodes buried directly in soils will vary depending upon the soil composition and will be excessive in chloride-containing soils. In quicksands consumption rates of approximately 0.35 kg $\text{A}^{-1} \text{y}^{-1}$ have been reported⁸¹, whilst in other soils consumption rates in the region of 1 kg $\text{A}^{-1} \text{y}^{-1}$ are possible. A lower consumption rate in the region of 0.1 to 0.25 kg $\text{A}^{-1} \text{y}^{-1}$ would be expected in a carbonaceous backfill correctly installed, in a soil of insignificant chloride content and the anode operating at a current density of 20 Am^{-2} . Very much higher apparent consumption rates would most likely be due to high local current densities caused when the anode is inadequately backfilled, partially submerged, or where it has become partially silted up.

The anode effectiveness is only as good as the anode connection and loss of insulation at this point by deep pitting of the HSI or penetration of the anode cable seal will bring about rapid failure. Hydrostatic pressure should be borne in mind when considering the seal required for any depth of water. The useful life of HSI anodes is usually considered at an end after a 33% reduction in diameter, but this depends upon the original diameter, the amount of pitting sustained and the mechanical stresses to be withstood. Thus doubling the cross-sectional area may more than double the effective life of the anode.

High Silicon/Molybdenum Iron

The addition of 1–3% Mo to HSI results in an improvement in maintaining a conducting oxide film in chloride-containing solutions above 200 p.p.m. or at temperatures of 38°C or above. However, the addition of Cr has resulted in even greater improvements. In seawater at 10 Am^{-2} the addition of Mo reduced the consumption rate from 0.22 to $0.15 \text{ kg A}^{-1} \text{ y}^{-1}$ at ambient temperatures and from 0.63 to $0.21 \text{ kg A}^{-1} \text{ y}^{-1}$ at 51°C ⁸⁵. Yet a considerably higher wastage rate of $0.9 \text{ kg A}^{-1} \text{ y}^{-1}$ at 10.8 Am^{-2} has been reported for the molybdenum-containing silicon iron in chloride-containing waters⁸¹.

High-Silicon/Chromium Iron (HSCI)

This alloy was first put into commercial use around 1959⁸⁵. Chromium, together with silicon, results in a film that has a high resistance to pitting in waters containing halide ions, and these alloys can be used in seawater or chloride-containing soils with confidence. A typical analysis is 14.5% Si, 0.75% Mn, 1.0% C, 4.5% Cr, remainder Fe. In the UK this anode is manufactured to BS 1591:1975 which permits a variation in silicon content of 14.25 to 15.25%, and that of chromium of 4 to 5%, with a maximum carbon content of 1.40%. The equivalent US standard is ASTM A 518-64 Grade 2 with a silicon content of 14.2 to 14.75% and a chromium content of 3.25 to 5.00%. Neglecting possible mechanical damage and anode/cable joint failure, it is possible, in view of the very minor pitting sustained in free suspension, for the anode to continue operating until totally consumed.

Comparative tests between HSI and HSCI in seawater at 93°C and 10.8 Am^{-2} showed consumption rates of $8.4 \text{ kg A}^{-1} \text{ y}^{-1}$ and $0.43 \text{ kg A}^{-1} \text{ y}^{-1}$, respectively⁸⁶. These figures show that the consumption rate of HSI when used in seawater without the addition of chromium may approach that of steel, but because of the very deep pitting and its fragility, it is in most cases inferior to steel. However, in fresh waters HSI has a far lower corrosion rate than steel. The consumption rate of HSCI freely suspended in seawater in the current density range 10.8 to 53.8 Am^{-2} increases from $0.33 \text{ kg A}^{-1} \text{ y}^{-1}$ at 10.8 Am^{-2} to $0.48 \text{ kg A}^{-1} \text{ y}^{-1}$ at 53.8 Am^{-2} . Direct burial in seawater silt or mud will also increase the consumption rate, with values of $0.7 \text{ kg A}^{-1} \text{ y}^{-1}$ at 8.5 Am^{-2} increasing to $0.94 \text{ kg A}^{-1} \text{ y}^{-1}$ at 23.4 Am^{-2} ⁸⁷.

HSCI anodes cannot be used in potable waters because of the possibility of chromium contamination.

A recent evaluation of HSCI anodes in different soil conditions has been conducted by Jakobs and Hewes⁸⁸. They report a consumption rate for different HSCI alloys in 3% NaCl, at a current density of 21.5 Am^{-2} , of between 0.32 and $0.87 \text{ kg A}^{-1} \text{ y}^{-1}$ depending upon the alloy composition; whilst in soils containing 2% SO_4^{2-} consumption rates varied between 0.29 and $0.53 \text{ kg A}^{-1} \text{ y}^{-1}$, again depending upon the alloy composition.

Improvements in anode construction have also been carried out to reduce the non-uniform material loss along the length of the HSCI anode, the so-called 'end effect' phenomenon. This involves the use of hollow, centrifugally

cast anodes of uniform wall thickness with a centrally located interior electrical connection⁸⁹. Care should be taken to ensure that the cable insulation and sheathing are adequate for use in an oxidising environment, in which chlorine evolution occurs.

Magnetite Anodes

Magnetite (Fe_3O_4) has been in use since the 1970s as a cathodic protection anode, although its use as anode material has been known for some time⁹⁰.

Magnetite has a melting point of 1540°C and can be cast using special techniques and with the addition of certain alloying elements⁹¹. The anodes are constructed from a cast alloyed magnetite shell, the centre of which is hollow. The internal surfaces of the magnetite shell are then lined with an electronic conductor so as to ensure a uniform distribution of current density over the external surface. This technique overcomes the longitudinal current attenuation that would occur because of the relatively high resistivity of magnetite (3.3 ohm m quoted by Linder⁹¹ and 0.8 ohm m by Kofstad⁹²).

In early magnetite anodes the internal lining consisted of a thin copper layer, but the poor electrical contact between the copper layer and the magnetite, together with the fact that the cable-to-anode connection was made at the anode head, resulted in a non-uniform current density on the external magnetite surface, which contributed, in part, to the poor performance reported for some of the early magnetite anodes. Subsequently, the manufacturers perfected a method of electrodepositing a lead alloy lining onto the internal magnetite surface with the cable-to-anode connection made at the mid point of the anode.

The central portion of the anode is filled with polystyrene and the anode cable attachment, whilst the remainder is filled with an insulating resin.

Magnetite anodes exhibit a relatively low consumption rate when compared with other anode materials, namely graphite, silicon iron and lead and can be used in seawater, fresh water and soils. This low consumption rate enables a light-weight anode construction to be utilised. For example, the anode described by Linder⁹¹ is 800 mm in length 60 mm in diameter, 10 mm wall thickness and 6 kg in weight.

Tests carried out in seawater over the current density range 30 to 190 Am^{-2} showed the consumption rate to be dependent upon current density, increasing from 1.4 to $4\text{ g A}^{-1}\text{ y}^{-1}$ over the current density range studied (with the recommendation that to achieve the required life, the current density should not exceed 115 Am^{-2})⁹³.

Later work by Jakobs and Hewes⁸⁸ indicated the consumption rate in seawater to be less than $1\text{ g A}^{-1}\text{ y}^{-1}$ at 21.6 Am^{-2} , whilst at 32.4 Am^{-2} a consumption rate of 12 to $41\text{ g A}^{-1}\text{ y}^{-1}$ was observed. Higher consumption rates were reported for magnetite anodes in soils containing 2% SO_4^{2-} ; namely $75\text{ g A}^{-1}\text{ y}^{-1}$ at current densities of 21.6 and 32.4 Am^{-2} , respectively. Jakobs⁹⁴ also conducted a survey of different anode systems in soils and found magnetite anodes after 2 years exposure and operating at a current density of 43 Am^{-2} to be in good condition with little evidence of attack.

Magnetite anodes can be operated at elevated temperatures up to 90°C, with the limitation in temperature being failure of the anode cable connection and not the magnetite itself.

The main disadvantages of magnetite anodes are that they are brittle, and susceptible to high-impact shocks, as is the case with silicon iron anodes, whilst some of the earlier anodes were subject to failure from thermal cycling^{10,91}. Indeed, one evaluation of magnetite anodes reports a high incidence of failure⁹⁴, and a more recent report⁹⁵ lists a number of failures of magnetite anodes when compared with other more conventional anode materials. Although these failures were mainly associated with poor installation practice and operation at current densities in excess of the manufacturers' maximum recommended values which are 77 Am⁻² for seawater and 30 Am⁻² for soils. Improvements in the anode design have now led to a more reliable anode with a decrease in the level of reported failures¹⁵⁸.

Magnetite may also be used in combination with lead or electrodeposited onto a titanium substrate⁹⁶. The latter anode system has been shown to exhibit good operating characteristics in seawater but at present it is only of academic interest.

Ferrite Anodes

Sintered and sprayed ceramic anodes have been developed for cathodic protection applications. The ceramic anodes are composed of a group of materials classified as ferrites with iron oxide as the principal component. The electrochemical properties of divalent metal oxide ferrites in the composition range 0.1MO–0.9Fe₂O₃, where *M* represents a divalent metal, e.g. Mg, Zn, Mn, Co or Ni, have been examined by Wakabayashi and Akoi⁹⁷. They found that nickel ferrite exhibited the lowest consumption rate in 3% NaCl (of 1.56 g A⁻¹ y⁻¹ at 500 Am⁻²) and that an increase in the NiO content to 40 mol%, i.e. 0.4NiO–0.6Fe₂O₃ reduced the dissolution rate to 0.4 g A⁻¹ y⁻¹ at the expense of an increase in the material resistivity from 0.02 to 0.3 ohm cm.

Ceramic anodes may be cast or sintered around a central steel core which acts as the electrical conductor. However, anodes produced in this form are brittle and susceptible to mechanical shock.

Ceramic anodes based on a plasma-sprayed ferrite coating on a titanium or niobium substrate have also been developed. These consist of plasma-sprayed lithium, nickel or cobalt ferrite on a machined Ti or Nb button-shaped substrate fitted into a plastic electrode holder⁹⁸. This method of anode construction is durable, and not as prone to mechanical damage as the sintered ceramic anode whilst the ceramic coating is abrasion resistant and has a long operational life. Kumar *et al.*⁹⁸ report a dissolution rate for a sprayed lithium ferrite of 1.7 g A⁻¹ y⁻¹ at a current density of 2 000 Am⁻² in seawater. The anode exhibited good performance with no damage on the ceramic coating observed during a two-month trial. However, the normal restrictions on operating voltages for titanium electrodes were still found to apply, with pitting⁹⁹ of the titanium substrate reported at 9.66 V vs. SCE.

Lead Materials

Investigations into the use of lead alloys for cathodic protection were made in the early 1950s¹⁰⁰⁻¹⁰² and a practical material had been developed by 1954. The general use of lead alloys in seawater had previously been established^{103, 104}.

The anodic behaviour of Pb varies depending upon the electrolyte composition and the electrode potential and has been the subject of a number of reviews^{10, 104, 105}. In NO_3^- , CH_3COO^- and BF_4^- solutions, lead will form highly soluble lead salts whilst in Cl^- and SO_4^{2-} solutions, insoluble lead salts are formed when Pb is anodically polarised,

In using metallic Pb as an anode the formation and maintenance of a hard layer of PbO_2 is essential, since it is the PbO_2 that is the actual inert anode, the Pb acting both as a source of PbO_2 and an electrical conductor. PbO_2 is relatively insoluble in seawater and its dissipation is more usually associated with mechanical wear and stress than electrochemical action.

In alkaline solutions approaching pH 10, PbO_2 is unsuitable for use, and for this reason it should be mounted clear of any calcareous deposit which may be formed on a cathodic area close to the anode: this deposit indicates the formation of alkali which may have a detrimental effect on the PbO_2 deposit.

Lead has found considerable use as an anode in a wide variety of electrochemical applications, with studies dating back to 1924¹⁰⁵⁻¹⁰⁷. Pure Pb has been tried as an anode in seawater but fails to passivate, since PbCl_2 forms beneath the PbO_2 and insulates the PbO_2 from the Pb substrate. The anodic behaviour of Pb in Cl^- solutions depends upon Cl^- ion concentration, the solution pH and the presence of passivating anions such as CO_3^{2-} , HCO_3^- and SO_4^{2-} . At low current densities and low Cl^- concentrations, dissolution of Pb will occur and a PbCl_2 deposit will not be formed at the anode. In high Cl^- concentrations and at high current densities the rate of formation of Pb^{2+} will be high enough for the solubility product for PbCl_2 to be exceeded, and PbCl_2 , not PbO_2 , will be deposited at the anode.

The formation of a PbO_2 coating on Pb when it is anodically polarised in Cl^- is achieved more readily by alloying lead with silver or other metals, or by incorporating inert conducting microelectrodes in the Pb surface.

Pb alloys have been investigated to determine their suitability as anodes for cathodic protection. Crennel and Wheeler¹⁰⁸ carried out tests on Pb-Ag alloys and found that Pb-1Ag was suitable for use in seawater providing that the current density did not exceed $100\text{--}200\text{ Am}^{-2}$, since at high current densities an insulating film formed. Other Pb alloys have been investigated, notably Pb-6-8Sb which required more than 200 Am^{-2} to passivate, whilst Pb-6Sb-10Sn exhibited a high corrosion rate¹⁰³. However, Morgan^{108, 109} found that Pb-6Sb-1Ag alloy gave a lower consumption rate and exhibited a harder PbO_2 film than Pb-6Sb or Pb-1Ag. Pb-6Sb-2Ag alloys are slightly better, but about 50% more expensive. More recent work¹¹³ has also shown that additions of Mn to Pb-2Ag alloys may have a beneficial effect on anode performance in seawater. The Pb-6Sb-1Ag alloy is commonly used where Pb-Ag anodes are specified. The results of tests on Pb-6Sb-1Ag given in Table 10.18 are of interest in recognising the scope

Table 10.18 Behaviour of Pb-6Sb-1Ag anodes

Resistivity of electrolyte at 35°C (ohm m)	Average wastage rate at 108 Am ⁻² (kg A ⁻¹ y ⁻¹)	Length of trial (days)	Note
0.163 (sea)	0.086	236	1
0.163 (NaCl)	1.99	1.75	2
0.5 (sea)	0.0145	234	1
0.5 (NaCl)	0.654	1.75	3
10 (sea)	23.80	5.75	4
10 (NaCl)	23.70	1.75	4
50 (sea)	0.10	236	5
50 (NaCl)	11.64	1.75	5

Notes: 1. Service indicates a practical consumption of between 0.057 and 0.114 kg A⁻¹y⁻¹. Under laboratory conditions PbO₂ has been formed at current densities as low as 21.6 Am⁻². Typical operating current densities are 54–270 Am⁻² at wastage rates of 0.045⁽¹¹⁴⁾ to 0.082 kg A⁻¹y⁻¹ (111).

2. Similar performance between 0.7 and 270 Am⁻²; formation of thin adherent film of PbO₂⁽¹¹²⁾.

3. Similar performance between 2.7 and 160 Am⁻²; thick nodules of PbO₂ in some areas; severe deterioration at 270 Am⁻² (113).

4. Tests have indicated failure to form PbO₂; rapid deterioration, although at 100 Am⁻² it slows down after several weeks. Increasing silver content results in some improvement⁽¹¹²⁾. Anode passivated in 0.163 ohm m water continues to operate whilst PbO₂ is undamaged⁽¹¹⁴⁾.

5. Above 22 Am⁻² deterioration rate may be low, but PbO₂ coating is poor and interspersed with PbCl₂.

of practical lead alloys in waters of differing resistivities.

In electrolytes containing both sulphate and chloride ions, the sulphate ion favours the formation of lead sulphate which is rapidly transformed to lead dioxide. The continuing satisfactory operation of the anode depends upon the initial conditions of polarisation. The lead dioxide is of better quality and more adherent when formed below 108 Am⁻², in solutions containing higher sulphate concentrations or when the water is agitated⁽¹¹⁰⁾.

It should be remembered that a minimum current density is necessary to ensure passivation of the anode and that anodes operating below this current density may experience rapid consumption rates. A minimum value of 32.3 Am⁻² is quoted by Barnard *et al.*⁽¹⁰³⁾. The consumption rate of lead silver is high in the initial stages of operation as can be seen from Table 10.18. However, the rate in seawater, taken over an extended period, is generally taken as 0.06 kg A⁻¹y⁻¹.

If a lead alloy is used as a ship's hull anode, consideration should be given both to the make-up of the water in which the anode is initially passivated and that in which it will normally operate. The same consideration will apply for static structures in estuarine waters.

It should be noted that lead dioxide will discharge if electronically connected to a more base material, when in an unenergised state. The reverse current leakage of a rectifier will allow this to happen to a small extent if the rectifier is faulty, with the consequent formation of lead chloride and corrosion of the anode.

Recent experience with Pb-6Sb-1Ag and Pb/Pt anodes operating in seawater at depths greater than 25 m has revealed a marked increase in consumption rate compared with that found on the surface. Hollandsworth and Littauer⁽¹¹⁵⁾ have calculated that on a fully formed anode at 400 Am⁻², only $6 \times 10^{-5}\%$ of the current is used to maintain the passive film, yet at a depth of 180 m this percentage increases to $2 \times 10^{-3}\%$, and results in a 30-fold increase in consumption rate. They propose that a combination of

the mechanical forces acting on the PbO_2 at increased depths, and the reduction in the evolution of chlorine, are responsible for the increased consumption rate. It is therefore recommended that lead anodes are not used at depths below 25 m.

Lead/Platinum Bi-electrodes

The insertion of platinum microelectrodes into the surface of lead and some lead alloys has been found to promote the formation of lead dioxide in chloride solutions^{116,117}. Experiments with silver and titanium microelectrodes have shown that these do not result in this improvement¹¹⁰. Similar results to those when using platinum have been found with graphite and iridium, and although only a very small total surface area of microelectrodes is required to achieve benefit, the larger the ratio of platinum to lead surface, the faster the passivation¹¹⁶. Platinised titanium microelectrodes have also been utilised.

Lead dioxide will readily form on lead with a platinum electrode as small as 0.076 mm in diameter¹¹⁶⁻¹¹⁸. It has been observed that the current density on the platinum is considerably less than on the lead dioxide once polarisation has been achieved, the proportion of current discharged from the platinum decreasing with increase in total current.

Additions of antimony, bismuth and tin to the lead appear to be detrimental. There is an indication that the addition of 0.1% Ag is almost as effective as 1% and additions as low as 0.01% has been utilised in practice. Dispersion-hardened lead alloys have been unsatisfactory, showing pronounced spalling in the direction of extrusion. Pb-0.1Te-0.1Ag has been also used with apparent success¹¹⁹.

A typical anode for practical use would be in the order of 25 to 48 mm in diameter, with hard platinum alloy pins of 0.50 mm diameter by 10 mm length, spaced every 150 to 300 mm and progressively positioned around the circumference¹²⁰. The pins are a press fit into holes in the lead or lead alloy (approximately 0.1 mm diametric interference) and lie flush with the surface. The lead is peened around the pins to improve the mechanical and electrical contact.

The action of platinum microelectrodes has been extensively studied^{10,105}. Trials carried out by Peplow¹²¹ have shown that lead/platinum bi-electrodes can be used in high velocity seawater at current densities up to 2000 Am^{-2} and that blister formation with corrosion under the blisters is decreased by the presence of platinum microelectrodes. The current density range in which the anode is normally operated is $200\text{--}750 \text{ Am}^{-2}$ with the maximum working current density quoted as 1000 Am^{-2} . The consumption rate of these anodes ranged from $0.0014 \text{ kg A}^{-1} \text{ y}^{-1}$ to $0.002 \text{ kg A}^{-1} \text{ y}^{-1}$ at 500 Am^{-2} , but increased to $0.003 \text{ kg A}^{-1} \text{ y}^{-1}$ at 2000 Am^{-2} ¹²¹.

The results of work in this field^{116,119,122,123} can be summarised as follows:

1. Pt acts as a stable electrode for nucleation of PbO_2 and limits PbCl_2 formation.
2. In the case of a lead anode (without a platinum microelectrode), the

PbO₂ thickens during prolonged polarisation with the consequent development of stresses in the film.

3. The stresses result in microcracks in the PbO₂, thus exposing the underlying lead, which corrodes with the formation of voluminous PbCl₂, resulting in blisters; the resistance of the anode increases and high voltages are required to maintain the current (if the voltage is maintained constant the current falls to a low value).

The platinum microelectrode appears to act as a potentiostat and maintains the potential of the Pb-solution interface at a crack at a value that favours the re-formation of PbO₂, rather than the continuous formation of PbCl₂ which would otherwise result in excessive corrosion.

It is known that an increase in the resistance of the electrode indicates that corrosion is taking place with the formation of an insulating film of a lead compound, and this is confirmed in practice by observation of the anodes, which reveal localised areas coated with white corrosion products, although the PbO₂ remains intact at other areas. However, it is possible that an insulating film forms over the whole surface thus isolating the conducting PbO₂ from the lead. Wheeler¹²⁴ suggested that the sole function of the platinum is to provide a conducting bridge between the lead and the PbO₂. It has been demonstrated that, although initially the PbO₂ nucleates at the surface of the platinum, the initially formed PbCl₂ is rapidly converted into PbO₂ that is in direct contact with the lead¹¹⁶.

The formation of PbO₂ is favoured in solutions containing passivating anions such as SO₄²⁻ and in chloride solutions of intermediate concentrations; very high and very low concentrations of chloride inhibit the formation of PbO₂. The platinum/lead bi-electrode performs best in seawater, and is not recommended for use in waters of high resistivity.

Lead/Magnetite Composites

It has been demonstrated that particles of conducting Fe₃O₄ in a Pb matrix can produce results similar to that of platinum, in acting as stable nucleation sites for PbO₂ formation¹²⁵. Composite Pb/Fe₃O₄ anodes containing 10, 15 and 20% Fe₃O₄ were prepared by mixing powders of the constituents (Pb 30 to 60 mesh, Fe₃O₄ 72 mesh), then compacting at a pressure of 300 MNm⁻²^{10, 126}. These anodes were found to operate successfully in both artificial seawater, resistivity 0.25 ohm m and in this water diluted with distilled water to give a higher resistivity of 10 ohm m.

In seawater the anodes were found to operate in the current density range 100–1 000 Am⁻², with a weight loss of 50 g A⁻¹ y⁻¹ recorded for a 20% composite anode at 300 Am⁻². No initial rise in voltage at a constant current density was observed, as is the case with Pb/Pt electrodes where the potential increases due to the formation of PbCl₂, with the steady-state potential of the anodes found to be dependent upon the Fe₃O₄ content. In fresh water solutions, composite anodes were also able to form a passivating PbO₂ film. Although an induction period was necessary before stabilisation was complete, in the case of a Pb–10% Fe₃O₄ composite, Hill reports that at current densities less than 150 Am⁻², the anodes were unable to stabilise.

Consumption rates similar to those in artificial seawater were reported for the Pb-20% Fe₃O₄ composites, which were found to give the optimum performance. However, in tap water with a high SO₄²⁻ and CO₃²⁻ concentration and low Cl⁻ concentration (36 ppm), consumption rates of 100 g A⁻¹ y⁻¹ were recorded.

Lead Dioxide On Other Substrates

Lead dioxide on graphite or titanium substrates has been utilised as an anode in the production of chlorate and hypochlorites¹²⁷ and on nickel as an anode in lead-acid primary batteries¹²⁸.

Lead dioxide on a titanium substrate has also been tested for use in the cathodic protection of heat exchangers⁸¹ and in seawater may be operated at current densities up to 1 000 A m⁻²¹²⁹. However, this anode has not gained general acceptance as a cathodic protection anode for seawater applications, since platinised Ti anodes are generally preferred.

Carbonaceous Materials

Carbon

The corrosion product is predominantly carbon dioxide, but considerable amounts of free oxygen are produced at the anode surface, particularly in fresh-water applications, and can attack both the carbon and any organic binders used to reduce its porosity. For this reason carbon anodes for underground service are used in conjunction with a carbonaceous backfill.

If all the oxygen produced were to combine with the carbon the maximum theoretical wastage rate would be of the order of 1 kg A⁻¹ y⁻¹¹³⁰. However, in practice the rate is usually of the order of 0.2 kg A⁻¹ y⁻¹, and in coke breeze may be as low as 0.05 kg A⁻¹ y⁻¹. In seawater, where chlorine is the predominant gas produced, to which carbon is immune, any oxygen formed will be quickly removed and the corrosion rate may be very low.

Graphite

Graphite is a denser crystalline form of carbon. Graphite anodes are prepared by heating calcined petroleum coke particles with a coal tar pitch binder. The mix is then shaped as required and heated to approximately 2 800°C to convert the amorphous carbon to graphite¹³¹. Graphite has now superseded amorphous carbon as a less porous and more reliable anode material, particularly in saline conditions.

The performance of graphite in seawater, where chlorine is the principal gas evolved, is considerably better than in fresh water where oxygen is produced. Graphite is immune to chlorine and has a long history in the chemical industry in this and similar applications¹³².

It is current practice to impregnate the graphite, traditionally with linseed oil, although synthetic resins are also successful. The concept behind impregnation is to reduce the porosity and hence inhibit subsurface gas evolution or carbon oxidation which would initiate spalling and early anode failure. Electrode processes occur to a depth of 0.5 mm below the surface of the anode and the true current density can be shown to be only 1/400th of the value indicated by the superficial geometrical area¹³³. Acidity has been found to increase the wear rate¹³⁴ and so has the presence of sulphate ions¹³⁵. Indeed, when buried in soils containing 2% SO_4^{2-} Jakobs and Hewes⁸⁸ report graphite consumption rates of $1.56 \text{ kg A}^{-1} \text{ y}^{-1}$ at 21.6 Am^{-2} , which is considerably higher than the theoretical maximum consumption rate. These factors must be considered with regard to the operating environment and the chemical treatment of backfill.

The material can be easily machined being a natural lubricant. It has a negligible contact resistance and it is relatively simple to make a sound cable joint, although the comments regarding cable/anode joints discussed under high-silicon iron also apply. The material can be d.c. welded under high pressure argon. It is brittle but a little more shock resistant than silicon iron, in that it can absorb energy by localised damage; it is of course a lighter material to handle.

The anode is not recommended for use in water at above 50°C , where the consumption rate increases rapidly and erratically. It is no longer the practice to use this material in cooling water plant where secondary attack from contact with the relatively noble pieces of anode may occur, should damage take place.

The wastage rate of graphite is lower in seawater at higher current densities because of the preferential evolution of chlorine. Table 10.19 gives some results obtained with graphite under different conditions. Results obtained with one particular installation using a 100 mm diameter anode 1 m in length operating at 6.9 Am^{-2} indicate a predicted life of 20 years¹³⁶.

Table 10.19 Performance of graphite

Environment	Wastage rate ($\text{kg A}^{-1} \text{ y}^{-1}$)	Current density (Am^{-2})	Reference
Backfill	0.9	10.8	80
Hot Water	0.9	—	108
Seawater	0.045	4.5–115	111
Seawater	Little	10.8	108
Fresh water	0.45	3.5	108
Fresh water	0.45	2.7	111
Mud	0.91–1.36	71	173

Graphite anodes when used in soils are invariably placed in a carbonaceous backfill. This helps to compensate for the lower electrical resistivity of graphite when compared with silicon iron. In such an environment, no build-up of a film of high resistance between the anode and backfill occurs, unlike silicon-iron anodes where the resistance can increase with time¹³⁷.

Failures of graphite anodes can occur by corrosion of the anode connection, i.e. high current densities at either end of the anode resulting in

excessive consumption rates often referred to as 'end effect' corrosion, sealant failure or surface contamination¹³⁸.

Conductive Polymers

A continuous polymer anode system has been developed specifically for the cathodic protection of buried pipelines and tanks. The anode, marketed under the trade name Anodeflex¹³⁹, consists of a continuous stranded copper conductor (6 AWG) which is encased in a thick jacket of carbon-loaded polymer, overall diameter 12.5 mm. To prevent unintentional short circuits an insulating braid is sometimes applied to the outer surface of the conductive polymer.

The anode may be operated in the temperature range -18°C to 65°C and at currents up to 0.05 A per linear metre in soil and 0.01 A per linear metre in water, which corresponds with an effective maximum current densities of 0.66 Am^{-2} in soil and 0.13 Am^{-2} in water. No precise details on the anode consumption rate have been provided by the manufacturer, but since the electroactive material is carbon the consumption rate would be expected to be of a similar order to that exhibited by graphite anodes.

The anode may be installed in conventional groundbeds or be laid in close proximity to the cathode, e.g. parallel to a pipeline route. The anode may be buried either directly in soil or in carbonaceous backfill. The major applications for this material are tank protection, internal protection, mitigation of poor current distribution and hot spot protection, i.e. to supplement conventional cathodic protection systems and provide increased levels of cathodic protection in areas that exhibit low levels of protection.

The disadvantage of this anode system for the cathodic protection of pipelines is that the anode length provided by one single connection to the d.c. power source is limited by the ohmic losses along the copper conductors. Thus, the required current output per unit length and soil resistivity are limiting factors and a number of anode connections may be required to protect long lengths of pipeline. The anode has a poor chemical resistance to oils and should not be used in situations where oil spillage may occur.

Carbonaceous Backfills

Coke breeze is used as an anode extender thus producing an anode with an enormous surface area, its main component being carbon. By virtue of its porosity it gives a large volume-to-weight ratio of conducting medium suitable for anodic conditions. This allows the economic extension of groundbed anodes both linearly, for decrease in resistance to ground, and volumetrically for longevity. The grading of the coke is of some importance in that too large a grade offers large local contact resistance, leading to uneven consumption, whilst an excessively fine coke leads to over-tight compaction and gas blocking (gaseous polarisation). Chemicals are sometimes added, e.g. slaked lime (5–10% by weight), to counteract the tendency to lose moisture by electro-osmosis, since it is essential that an aqueous electrolyte is present to replace water consumed in the anodic reaction and conduct the

current to the protected structure. The alkaline material also serves to neutralise the anodically formed acid. Calcium sulphate is sometimes used in very dry conditions.

In using coke breeze the consumption of the primary anode is reduced, as the majority of the conduction from the anode to the coke breeze is electronic rather than electrolytic. The electrochemical and physical nature of the coke results in the dispersion of the anode reaction (formation of CO_2 and O_2) over a large surface area, thus reducing attack on the primary anode. The coke is oxidised primarily to carbon dioxide, which in a suitable groundbed will escape into the atmosphere together with any oxygen formed. If all the oxygen reacted, the coke consumption would be $1.02 \text{ kg A}^{-1} \text{ y}^{-1}$, but in practice consumption can be of the order of $0.25 \text{ kg A}^{-1} \text{ y}^{-1}$ ¹³⁷, depending upon the environment.

Some typical properties of coke breeze and similar materials are shown in Tables 10.20 to 10.22. The densities given in Table 10.20 are for bulk material and are dependent upon grading. Flake graphite is not recommended for use in groundbeds as it tends to conglomerate and prevent gas emission.

Table 10.20 Densities of backfill

<i>Backfill in bulk</i>	<i>Density range kg m⁻³</i>	<i>Typical density kg m⁻³</i>
Coal coke breeze	650–800	690
Calcined petroleum coke granules	700–1 100	720–850
Natural graphite granules	1 100–1 300	—
Man-made graphite, crushed	1 100–1 300	—

Table 10.21 Typical coal coke specification for cathodic protection⁽¹⁶⁹⁾

To pass 16 mm screen	100%
To pass between 16 mm and 8 mm screen	8.9–9.8%
To pass between 8 mm and 1 mm screen	78–90%
To pass 1 mm screen	1–14%
Fixed carbon	82.7 min to 91% max
Volatile matter	0.1%
Ash	8.6%
Moisture	5% max, typically 4%
Sulphur	1.2% max, typically
Phosphorus	0.42–0.7%
Resistivity (uncompacted)	0.55 ohm m max, (typically 0.35 ohm m)
Specific gravity	1.4

Table 10.22 Resistivities of carbonaceous backfills (ohm metre)

<i>Material</i>	<i>Dry</i>	<i>Tamped</i>	<i>Wet</i>
Coal coke	0.55	0.45	0.15
Graphite granules	1.50	1.20	0.20

When coke breeze is tamped down the correct pressure to aim for is approximately 15 Nm^{-2} . This will ensure integrity of the groundbed whilst in operation, remembering that it will be reducing in volume by chemical oxidation. A pressure of this magnitude will reduce the initial bulk resistivity of the coke.

The usual main object in using coke breeze is to lower the resistance of the anode to remote earth, with the coke cross-section, in a typical groundbed, normally about $300 \times 300 \text{ mm}$. In fresh-water soil conditions, the higher than average current density at the ends of the primary anodes can be prevented by not exceeding an anode spacing of twice its length. This depends entirely on the care taken in preparation of the groundbed assembly and ratio of the anode/coke resistance to the anode/electrolyte resistance. As the electrolyte resistance decreases, with a consequent increase in current density at the ends of the primary anodes, either a reduction in anode spacing or increase in backfill cross-section should be considered, particularly in foreshore groundbeds where the electrolyte resistivity will be of similar magnitude to that of the backfill.

In practice resistivities between 0.08 and 0.29 ohm m have been recorded on coke breeze samples used in typical groundbeds. The effect of pressure on the measured value for resistivity of different coke samples has also been reported elsewhere^{140, 141}. The resistivity of bulk metallurgical coke is given as 0.024 ohm m with a slightly lower value of 0.020 ohm m at a pressure of 0.43 Nm^{-2} , whilst in calcined fluid petroleum coke at zero applied pressure the resistivity was 0.02 ohm m , which decreased to 0.002 ohm m when tested at an applied pressure of 1.31 MNm^{-2} .

Calcined petroleum coke breeze with a high fixed carbon content of 99% is used in deepwell applications. The material has a low particle size and, with suitable additives, may be converted into a slurry and pumped into a borehole. The sulphur content of this material is high (1.4%), yet moisture (0.2%), ash (0.4%) and volatiles (0.4%) are low. The typical resistivity of this material is 0.15 ohm m .

A petroleum coke with round grains is available specifically for borehole cathodic protection applications¹⁴². The round grains ensure high porosity and enable gas to escape, allowing the coke to sink to the base of the borehole. This material has a higher bulk density than petroleum coke (1.185 kg m^{-3}) which enables it to sink to the bottom of the borehole, yet a lower fixed carbon content (93%), with higher ash (2.06%) and sulphur (5.3%) contents. The resistivity of this material is quoted as 0.1 ohm m .

Anodes used for the Cathodic Protection of Reinforced Concrete Structures

The corrosion of reinforcing steel due to chloride contamination in concrete is an increasingly serious problem, and interest in cathodic protection as a means of mitigating corrosion on reinforced steel has become of some importance in recent years.

Reinforced concrete structures that are fully immersed or buried in a corrosive environment may generally be protected using conventional cathodic

protection groundbed design. However, for the cathodic protection of above-ground reinforced concrete structures, e.g. bridge decks, jetties, tunnel parking garages, and certain concrete buildings, a number of specific anode systems have been developed. These are applied directly on to the concrete surface and often consist of a primary and secondary anode.

The various anode systems used specifically for reinforced concrete cathodic protection have been discussed in recent literature^{144, 145, 166} and will now be summarised.

Conductive Overlay Systems

Some of the early systems were based on the use of silicon iron primary anodes and a coke breeze/asphaltic cement (85%/15%) mix as the secondary anode to ensure uniform current distribution¹⁴³. The silicon iron anodes were held in position using a non-conductive epoxy, then covered with a conductive cement. Fromm¹⁴⁶ has investigated the performance of different coke breeze/asphalt mixes, and developed a mix containing only 45% coke breeze which had a resistivity of 0.03 ohm m and a voids content of 5%. This was reported to give good results. The conductive mix was then applied over the primary anodes, either silicon iron or graphite, to a total thickness of 50 mm, then given a protective top coat.

Schutt¹⁴⁷ reported that the coke breeze specification and conditions in which the mix is prepared are important factors in determining the optimum operation of the conductive cement mix, whilst further details on the coke breeze asphalt mix composition are given by Anderson¹⁴⁸. Conductive concrete mixes, with a polymer binder have also been developed as an anode system specifically for reinforced concrete cathodic protection systems¹⁴⁹.

Conductive overlay systems are not practical propositions on vertical surfaces or surfaces where weight restrictions are important. However, they are proven cathodic protection systems, and should be considered in conjunction with other reinforced concrete cathodic protection system anodes.

Conductive Polymers

A conductive polymer electrode has been designed specifically for the cathodic protection of steel reinforcing bars in concrete and is marketed under the trade name Ferex¹⁵⁰. The anode consists of a 16 AWG stranded copper conductor surrounded by a carbon-loaded polymeric coating similar to that used on the Anodex system¹³⁹ to provide a nominal anode diameter of 8 mm¹⁵¹. The manufacturer claims that at the maximum recommended current density of 0.08 Am⁻² the anode life in concrete will be 32 years with a proportionately longer life at lower current densities.

The major electrochemical reaction at the anode surface is oxygen and chlorine evolution coupled with oxidation of the active carbon to carbon dioxide. Eventually all the carbon is removed from the anode coating and this allows perforation of the copper conductor leading to ultimate anode failure.

The anode is fixed to the concrete using non-metallic fixings and may be supplied as a prefabricated mesh or more often as a continuous anode strand which is laid over the surface of the structure to be protected. The spacing between the anode strands may be adjusted to give the required current distribution and current density per unit area of concrete necessary to provide cathodic protection to a particular structure.

A number of anode connections will be made to the d.c. power source using proprietary splice kits (approximately one for every 60–80 m² of concrete to be protected). This will provide redundancy for anode failure and reduce ohmic losses along the anode cable. Care must also be taken not to expose the copper conductor during installation or anode failure could take place. Once fitted to the concrete surface a 15 mm thick cementitious overlay is applied above the anode mesh, as recommended by the anode manufacturer, although thickness of up to 35–40 mm have been applied in some instances.

Failures due to delamination of the gunite coating have been reported in the USA, but have not been observed to any significant extent in Europe¹⁶⁸, although some early failures of the anode system have been associated with high local current densities in areas of low concrete cover and high moisture or salt content¹⁶⁶. The major application of this anode system is therefore on structures that are relatively dry with a uniform current requirement.

Slotted Anode Systems

These consist of a number of parallel slots cut into the concrete surface. Each slot is then filled with a secondary anode of carbon/graphite fibres embedded in a conductive polymer grout. The current to each of these secondary anode systems is provided by a primary anode of platinised niobium wire placed in slots filled with conductive polymer which acts as the primary anode, these slots intersecting each slot of graphite fibre/conductive polymer at right angles.

These systems have not been installed to any significant extent and have now been superseded by conductive paints, conductive polymers or titanium mesh anode systems.

Conductive Paints

Conductive paints (resins) have recently been used for the cathodic protection of steel reinforcing bars in concrete, but they are always used in conjunction with a primary anode material, e.g. platinised-niobium or platinised-titanium wire or a conductive polymer rod.

Brown and Fessler¹⁵² have conducted a laboratory evaluation of conductive mastics that can be brushed or sprayed onto the concrete surface to achieve the necessary thickness. However, the most extensive study on conductive paints for cathodic protection purposes has been undertaken by the Federal Highway Authority¹⁴⁹. A total of nine commercially available resins were evaluated in this work. It was shown that neither thermal cycling, freeze thawing nor the application of cathodic protection currents

resulted in any deterioration of the most successful paint system which was designated Porter XP90895, but now referred to as DAC-85, a solvent based acrylic mastic containing graphite. Minor failures with this system have been reported but only in localised areas with a high chloride contact. The anode system generally consists of platinised titanium or niobium wire laid in strips with the layers of carbon fibre interleaved between the strips. The paint is then mixed and applied on site. The paint consists of blends of resin and fine particles of coke. The performance of some paint systems is poor because of attempts to operate the anodes at currents in excess of 0.1 Am^{-2} .

The advantages of conductive paints are that they are easy to apply and a concrete overlay is not required. They can be applied to complex shapes and are not a problem where weight restrictions are imposed.

Mixed Metal Oxide Coated Titanium Mesh

The most recently developed anode for the cathodic protection of steel in concrete is mixed metal oxide coated titanium mesh¹⁵³⁻¹⁵⁵. The anode mesh is made from commercially pure titanium sheet approximately 0.5–2 mm thick depending upon the manufacturer, expanded to provide a diamond shaped mesh in the range of 35×75 to 100×200 mm. The mesh size selected is dictated by the required cathode current density and the mesh manufacturer. The anode mesh is supplied in strips which may be joined on site using spot welded connections to a titanium strip or niobium crimps, whilst electrical connections to the d.c. power source are made at selected locations in a suitably encapsulated or crimped connection. The mesh is then fitted to the concrete using non-metallic fixings.

The active coating consists of a thermally deposited mixed metal oxide coating, the composition of which is considered proprietary information, although it is known that certain filler materials, e.g. Ta, may be added to the mixed metal oxide to reduce the precious metal content of the coating, and hence the cost of the anode.

The coating composition is iridium-rich to favour oxygen rather than chlorine evolution, and to assist in reducing the formation of acidic conditions at the anode-concrete interface.

It has been shown that the evolution of chlorine can result in the formation of an equivalent quantity of acid as that generated by oxygen evolution, because of the reaction between chlorine and water to form hydrochloric acid and hypochlorite¹⁵⁶. The latter is a strong oxidising agent and may have a detrimental effect on the concrete surrounding the anode mesh. Recent work has shown that acid attack on the concrete surrounding the mesh is limited with 0.2 mm recorded after 1.5 years at an anode current of 0.76 Am^{-2} which corresponds to only 1 mm after 25 years at a current density of 0.2 Am^{-2} ¹⁵⁶.

The current density applied to the electroactive coating has been set at 0.1 Am^{-2} , whilst for short-term polarisation current densities up to 0.2 Am^{-2} may be applied. However, certain anode manufacturers now state that a maximum current density of 0.2 Am^{-2} may be used for long-term polarisation and 0.4 Am^{-2} for short term use.¹⁵⁷ The current density range is

limited by the concrete and the need to reduce the level of degradation at the anode-concrete interface. Indeed, for an anode current density of 0.2 A m^{-2} , the life of the coating would be 30–50 years, based on a consumption rate of $87 \text{ mg A}^{-1} \text{ y}^{-1}$ and a mixed metal oxide coating thickness of 5 gm^{-2} .¹⁵⁷

The material once installed is then covered with a concrete coating, the minimum thickness of cover above the anode mesh is quoted as 10 mm, but 15 mm is preferred.

The anode voltage must be limited to 10 V to avoid damage to the titanium mesh, whilst cementitious overlays with a fluoride or bromide content must be avoided. However, in practice because of the relatively large anode surface and low current required systems generally operate at approximately 2–3 V. Low iron levels in the aggregate must also be maintained to avoid staining and possible inclusion of iron in the titanium oxide film. The mesh is light, nominally in the range $0.1\text{--}0.25 \text{ kg m}^{-2}$ dependent upon mesh type, so the only structural limitation is the weight of the cementitious overlay.

Reactive Metals

Aluminium

This is not often considered for use as an impressed-current anode, although it has found limited use in fresh-water tank protection, particularly where weight is a problem^{159–161}. To reach the required circuit resistance in high resistivity waters, it is necessary to use long extrusions of the order of 20 mm in diameter. The alloys H14 and H15 have been used for this purpose, pure Al being preferred in seawater¹⁰⁸. For tank protection the life of the anode is very much dependent on the extent of pitting. Necking can be a problem if the water level drops below part of the anode for long periods. The wastage rate in this area can be twice the normal.

In fresh water, voluminous corrosion products (namely $\text{Al}(\text{OH})_3$) can cause quite large increases (two-fold or more) above the initial anode/electrolyte resistance. This product, whilst not toxic, could prove an embarrassment in potable waters. Resistive polarisation is negligible in seawater use. The extent of the scale formation is a function of the nature of the water under consideration. Theoretically pure aluminium would be expected to dissipate of the order of $2.9 \text{ kg A}^{-1} \text{ y}^{-1}$, although a reasonably large safety factor should be used when considering anode integrity. Aluminium has also been successfully utilised as a trailing wire anode for the protection of ships, but this is no longer considered a practical application.

Zinc

Zinc is seldom used as a power-impressed anode. It may be a convenient way of achieving a high initial current density, particularly where descaling is involved, but it does, of course, require the anode to be locally insulated from the cathode. Used as a power-impressed anode the energy rate per

unit energy tends towards the theoretical value of $10.7 \text{ kg A}^{-1} \text{ y}^{-1}$ instead of the usual 90% efficiency when used as a galvanic anode.

In recent years, there has been interest in using zinc as a power-impressed anode for the cathodic protection of steel in concrete. The zinc is flame sprayed onto a grit blasted concrete surface to a final film thickness of approximately $250 \mu\text{m}$. A primary anode is necessary. Early systems used brass plates as the primary anode, but more recent systems used platinised titanium or niobium wire anodes as the primary current conductor.

The reason for the use of zinc as a power-impressed rather than a sacrificial anode is that the high concrete resistivity limits the current output, and a higher driving voltage than that provided by the e.m.f. between zinc and steel in concrete is used to provide the necessary current output. No cementitious overlay is required, although it may be advisable to paint the top surface of the sprayed zinc to prevent atmospheric corrosion of the zinc anode.

Summary

A comparison of typical properties of cathodic protection materials is given in Table 10.23, but is by no means comprehensive. It is obvious that the modification of an alloy, environment or other important factors will be reflected in the life and output characteristics. In some cases the maximum voltages and current densities recommended can be vastly exceeded. In others, particularly where abnormal levels of environmental dissolved solids are met, factors of safety should be applied to modify the proposed figures. Acceptance of a much reduced or uncertain life, weighed against a possible economy, may also influence the chosen working limits. For example, the life of ferrous alloy anodes may, in practice, be only two-thirds of that expected because of preferential attack eventually leading to disconnection of all or part of the anode from the source of e.m.f.

Table 10.23 must be taken only as a guide and interpreted in the best manner available, preferably using experience in that particular environment or operational requirement. Table 10.23 should be consulted in conjunction with the text and references, specifically those covering the whole range of cathodic protection anodes^{10, 163, 164, 167}. Consideration must be given to practicability, the factor of safety required, the environment, physical and electromechanical hazards, maintenance, operation, installation, availability, cost and the economics of replacement¹⁶².

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Table 10.23 Comparison of typical properties of cathodic protection anode materials

	Platinised tantalum	Platinised niobium	Platinised titanium	Platinum	Thermally deposited noble metal oxide on titanium	High-silicon/chromium iron
Approximate consumption $\text{kg A}^{-1} \text{y}^{-1}$	See Pt	See Pt	See Pt	8 to 18 $\times 10^{-6}$ B	0.5 to 6 $\times 10^{-6}$ B	0.25-1.0 B
Suggested minimum factor of safety on cross-sectional area	1.2	1.2	1.2	1.2	1.2	1.8
Max recommended current density (seawater Am^{-2})	2 000	2 000	1 000	B	600	120
Max recommended current density (fresh water Am^{-2})	B	B	B	B	100	120
Max recommended current density (soil Am^{-2})	B	B	B	B	B	60
Max recommended voltage (seawater)	B	B	8	D, G	8	D
Max recommended voltage (fresh water)	B	B	B	D, G	B	D
Specific resistivity 20°C $\text{ohm m} \times 10^{-8}$	12.5	15.2	48.2	9.85	48.2	72
Density (kg m^{-3})	16 600	8 750	4 150	21 450	—	7 000
Tensile strength (approx) (Nmm^{-2})	1 260	240 390	200	250 K	200	110
Hardness (approx)	80-100 HV	75-95 HV	—	200-400 HV	6 Mohs	520 HB
<i>General uses</i>						
Marine environment	YES	YES	YES	NO(M)	YES	YES(M)
Potable waters	YES	YES	YES	NO(M)	YES	NO(M)
In carbonaceous backfill	YES	YES	NO(M)	NO(M)	YES	YES
Buried directly in soil	NO(M)	NO(M)	NO(M)	NO(M)	NO(M)	YES
High-purity liquids	YES	YES	NO(M)	NO(M)	YES	NO

Notes: A Used with carbonaceous backfill, see text — depends on water resistivity/backfill resistivity

B See text

C Normal maximum longitudinally

D Limited by local or environmental safety requirements regarding apparatus and/or earth voltage gradient regulations

E Minimum current density to ensure passivation 50 Am^{-2} F Resistivity of PbO_2 , 10-100 ohm m

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Table 10.23 Comparison of typically properties of cathodic protection anode materials

High-silicon/ iron	Magnetite	Steel	Iron	Cast iron	Pb-65b- I Ag	Lead/ platinum	Graphite	Aluminium	Zinc	Coke breeze
0.25-1.0 B	0.001-0.04 B	6.8-9.1	Approx 9.5	4.5-6.8	0.09 B	0.09 B	0.1-1.0 B	2.0	10.8	0.5
1.8	1.2	1.8	1.8	1.8	1.5	1.5	1.5	2	1.2	1.5
N	77	L	L	L	200 E	500 E	30	20	20	—
120	—	L	L	L	—	—	2.5	20	20	—
60	30	5	5	5	—	—	10 A	2.5	2.5	2.6
D	D	D	D	D	D	D	D	D	D	—
D	D	D	D	D	—	—	D	D	D	—
72	8×10^7	17	12	55	25 F	22 C	700 C	27	6.2	B
7 000	4 750	7 700	7 820	7 100	10 900	11 300	1 560	2 700	7 400	B
130	—	500	300	150	30	25	28	85	—	—
						25	28	85		
450 HB	—	130-160 HB	120-170 HB	140-170 HB	13-10.7 HB	4 HB	80 SHORE	—	—	—
NO	YES	YES	YES	YES	YES	YES	YES	NO(N)	YES	YES
YES	YES	NO	NO	NO	NO	NO	YES	YES	NO	NO
YES	YES	YES	YES	YES	NO	NO	YES	NO	NO	—
YES	NO(M)	NO(M)	NO(M)	NO(M)	NO	NO	NO(M)	NO(M)	NO(M)	YES
NO	NO	NO	NO	NO	NO	NO	NO	NO(M)	NO	NO

G Voltage on Pt 1.35 V minimum

H Electrodeposited

K 50% cold rolled

L If in free suspension in moving water, no limit, local effects under high current density may increase wastage rate*

M May be used in the environment under special circumstances

N High consumption rate in this environment

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10.4 Practical Applications of Cathodic Protection

The complexity of the systems to be protected and the variety of techniques available for cathodic protection are in direct contrast to the simplicity of the principles involved, and, at present the application of this method of corrosion control remains more of an art than a science. However, as shown by the potential-pH diagrams, the lowering of the potential of a metal into the region of immunity is one of the two fundamental methods of corrosion control.

In principle, cathodic protection can be used for a variety of applications where a metal is immersed in an aqueous solution of an electrolyte, which can range from relatively pure water to soils and to dilute solutions of acids. Whether the method is applicable will depend on many factors and, in particular, economics – protection of steel immersed in a highly acid solution is theoretically feasible but too costly to be practicable. It should be emphasised that as the method is electrochemical both the structure to be protected and the anode used for protection must be in both metallic and electrolytic contact. Cathodic protection cannot therefore be applied for controlling atmospheric corrosion, since it is not feasible to immerse an anode in a thin condensed film of moisture or in droplets of rain water.

The forms of corrosion which can be controlled by cathodic protection include all forms of general corrosion, pitting corrosion, graphitic corrosion, crevice corrosion, stress-corrosion cracking, corrosion fatigue, cavitation corrosion, bacterial corrosion, etc. This section deals exclusively with the practical application of cathodic protection principally using the impressed-current method. The application of cathodic protection using sacrificial anodes is dealt with in Section 10.2.

Structures that are Cathodically Protected

The following structures are those which in given circumstances can benefit from the application of a cathodic-protection system:

Underground and underwater Underground fuel/oil tanks and pipelines; water, fire protection, gas and compressed underground air distribution schemes; underground metallic sewers and culverts; underground communication and power cables; deep wells; other buried tanks and tanks in

Table 10.24 Methods of application of cathodic protection

<i>Method</i>	<i>Characteristics</i>	<i>Anode materials*</i>	<i>Current source</i>	<i>Installation</i>	<i>Possibilities of secondary interaction in foreign structures</i>
Sacrificial anodes	Metal protected by sacrificial wastage of more electronegative metal	Magnesium, aluminium or zinc (iron for copper and copper alloys)	Faradaic equivalent of sacrificial metal—in practice the efficiency is seldom 100%	Extremely simple	Very improbable providing anodes properly located with respect to surface being protected
Impressed current ('power impressed')	Impressed currents using transformer-rectifiers, or any other d.c. source	Carbon, silicon-iron, lead-platinum, platinised titanium, platinised niobium, scrap iron, platinum metal oxides deposited on a titanium substrate	Source of low-voltage d.c. This may be generated or drawn from transformer-rectifier fed from main supplies	More complex	Very significant especially in built-up areas
Stray current ('drained current')	Buried structures bonded into traction system in such a way as to receive impressed-current protection	Bonded directly into stray d.c. supply	Drained from d.c. traction or stray-current supply	Simple	Stray-current effects are basically associated with primary power supply

* For protection of ferrous structures.

Table 10.24 (continued)

<i>Method</i>	<i>Application for which scheme is economical</i>	<i>Major limitations</i>	<i>Potential distribution</i>	<i>Current limitation</i>
Sacrificial anodes	Small land based schemes and for avoidance of interaction problems. Marine structures, e.g. offshore platforms	High soil/water resistivities and small driving e.m.f. may require a large number of anodes	Reasonably uniform	Cannot be applied in high-resistivity environments
Impressed current ('power impressed')	Especially suited to large schemes	Impracticable for small schemes on account of high installation costs Requires an external power source	Varies—maximum at drainage point falling towards remote points, but not below the optimum potentials for protection, i.e. in most cases the potential -0.85 V	Can be used in high-resistivity environments
Stray current ('drained current')	Applicable only in proximity to stray d.c. areas			

contact with the ground; tower footings, sheet steel piling and 'H'-piling; piers, wharfs and other mooring facilities; submarine pipelines; intake screens (condenser/circulating water); gates, locks and screens in irrigation and navigation canals; domestic oil distribution lines or central heating systems.

Above ground (internal surfaces only) Surface and elevated water storage tanks; condensers and heat exchangers; hot-water storage tanks, processing tanks and vessels; hot- and cold-water domestic storage tanks; breweries and dairies (pasturisers).

Floating structures Ballast compartments of tankers; ships (active and in 'mothballs'); drilling rigs; floating dry-docks; barges (interior and exterior); dredgers; caisson gates; steel mooring pontoons; navigation aids, e.g. buoys.

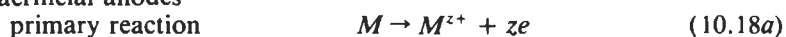
Type of System

The use of an impressed-current system or sacrificial anodes will both provide satisfactory cathodic protection, but each has advantages and disadvantages with respect to the other (Table 10.24).

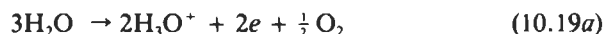
Sacrificial anodes and power-impressed anodes have been dealt with in detail in the previous sections, but some further comment is relevant here in relation to the choice of a particular system for a specific environment. In this connection it should be noted that the conductivity of the environment and the nature of the anode reactions are of fundamental importance.

The main anodic reactions may be summarised as follows:

Sacrificial anodes



Impressed-current anodes



and/or



or, in the case of graphite anodes



It should be noted that when metals like zinc and aluminium are used as sacrificial anodes the anode reaction will be predominantly 10.18a and 10.18b, although self-corrosion may also occur to a greater or lesser extent. Whereas the e.m.f. between magnesium, the most negative sacrificial anode, and iron is ≈ 0.7 V, the e.m.f. of power-impressed systems can range from 6 V to 50 V or more, depending on the power source employed. Thus, whereas sacrificial anodes are normally restricted to environments having a resistivity of $< 6000 \Omega \text{ cm}$ there is no similar limitation in the use of power-impressed systems.

In the case of sacrificial anodes the electrons that are required to depress the potential of the structure to be protected are supplied by reaction 10.18a,

and providing the metal ions can diffuse away from the structure before they react with water to form insoluble hydroxides the reaction will be unimpeded and will take place at a low overpotential. If, however, the metal hydroxide precipitates on the surface of the metal as a non-conducting passive film the anode reaction will be stifled and this situation must be avoided if the anode is to operate satisfactorily. On the other hand, in the case of non-reactive impressed-current anodes, rapid transport of the reactants (H_2O and Cl^-) to, and the reaction products (O_2 and Cl_2) away from, the anode surface is essential if the anode reaction is to proceed at low overpotentials. This presents no problems in sea-water, and for this reason the surface areas of the anodes are comparatively small and the anode current densities correspondingly high. Thus, in sea-water inert anodes such as platinised titanium and lead-platinum can operate at $\approx 500\text{--}1\,000\text{ Am}^{-2}$, since the anode reaction 10.19b occurs with little overpotential, and there is rapid transport of Cl^- to and Cl_2 away from the anode surface. In this connection it should be noted that even in a water of high chlorinity such as sea-water, oxygen evolution should occur in preference to oxygen evolution on thermodynamic grounds. This follows from the fact that the equilibrium potential of reaction 10.19a in neutral solutions is 0.84 V, whereas the corresponding value for 10.19b is 1.34 V, i.e. 0.5 V higher. However, whereas the chlorine evolution reaction occurs with only a small overpotential, very appreciable overpotentials are required for oxygen evolution, and this latter reaction will occur therefore only at high current densities. Even in waters of low salinity chlorine evolution will occur in preference to oxygen evolution at low overpotentials.

In the protection of pipelines or other underground structures the anode reaction is dependent on diffusion of water to the anode surface and oxygen and CO_2 away from it, and since these processes do not occur with the same mobility as in water it is necessary to use a very large surface area of anode and a corresponding low current density. For this reason the actual anode is the carbonaceous backfill, and graphite or silicon-iron anodes are used primarily to make electrical contact between the cable and the backfill. It can also be seen from reaction 10.19a that the products of the oxidation of water are oxygen and the hydrated proton H_3O^+ , which will migrate away from the anode surface under the influence of the field, thus removing two of the three water molecules that participate in the reaction, and this will tend to dehydrate the groundbed. This difficulty can be overcome, when feasible, by locating the groundbed below the water table.

Sacrificial Anode Systems

Advantages No external source of power is required; installation is relatively simple; the danger of cathodic protection interaction is minimised; more economic for small schemes; the danger of over protection is alleviated; even current distribution can be easily achieved; maintenance is not required apart from routine potential checks and replacement of anodes at the end of their useful life; no running costs.

Disadvantages Maximum anode output when first installed decreasing with

time when additional current may be required to overcome coating deterioration; current output in high resistivity electrolytes might be too low and render anodes ineffective; large numbers of anodes may be required to protect large structures resulting in high anode installation and replacement costs; anodes may require replacement at frequent intervals when current output is high.

Impressed-current Systems

Advantages One installation can protect a large area of metal; systems can be designed with a reserve voltage and amperage to cater for increasing current requirement due to coating deterioration; current output can be easily varied to suit requirements; schemes can be designed for a life in excess of 20 years; current requirements can be readily monitored on the transformer-rectifier or other d.c. source; automatic control of current output or of the structure potential can be achieved.

Disadvantages Possible interaction effects on other buried structures (Section 10.6); subject to the availability of a suitable a.c. supply source or other source of d.c.; regular electrical maintenance checks and inspection required; running costs for electrical supply (usually not very high except in the case of bare marine structures and in power stations where structures are often bare and include bimetallic couples); subject to power shutdowns and failures.

Hybrid Systems

Offshore structures are often protected by hybrid systems using both sacrificial anodes and impressed-current. These have the advantage that protection of the steel by the sacrificial anodes will be effective as soon as the platform enters the sea, which is particularly advantageous since some time may elapse before the d.c. generators required for the impressed-current system are operating. Further details are given in Section 9.4, Design in Marine and Offshore Engineering.

Stray Current or Forced Drainage

Stray current schemes are relatively rare in occurrence in the UK as few localities now have widespread d.c. transport systems. Such systems are extensively used in overseas countries where d.c. transport systems are in use, i.e. Australia and South Africa. Where stray current can be employed it is normally the most economical method of applying cathodic protection since the power required is supplied gratis by the transport system.

In such systems it is necessary to provide a metallic bond between the pipeline and the negative bus of the railway substation. By providing such a bond the equivalent of a cathodic-protection system is established whereby current discharged from the traction-system rails is picked up by all portions of the

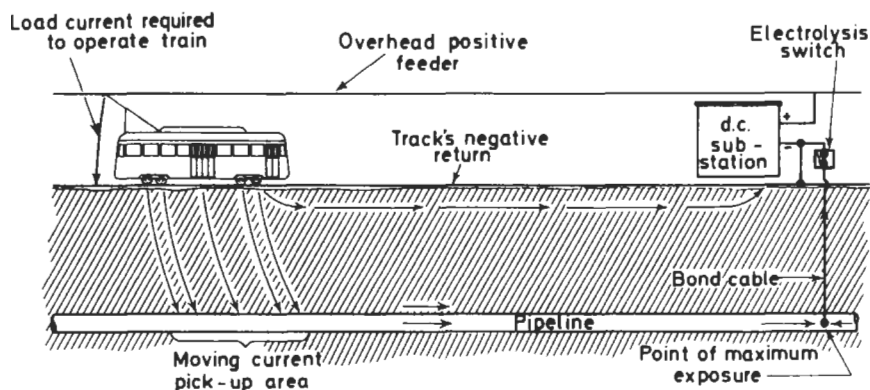


Fig. 10.21 Bond between pipeline and d.c. substation

pipeline and drained off via the bond. The bond must have sufficient carrying capacity to handle the maximum current drained without damage. In order to ensure that the direction of current flow in the bond does not reverse, it is normal to employ a reverse-current prevention device or 'electrolysis switch'. This may take the form of a relay-actuated contactor which opens automatically when the current reverses. Diodes may also be used as blocking valves to accomplish the same purpose. They are wired into the circuit so as to ensure that current can flow to the negative busbar system only. Sufficient diodes must be used in parallel to handle the maximum amount of current anticipated. Also the inverse voltage rating of the diodes must be sufficient to resist the maximum reverse voltage between the negative busbar and pipeline (Fig. 10.21).

Design of a Cathodic-protection System

To enable an engineer to design a cathodic-protection scheme, consideration should be given to the following points (see also Table 10.25).

Good practice in modern underground or underwater structures involves the use of good coatings in combination with cathodic protection. With a well-coated structure the cathodic-protection system need only protect the minute areas of steel exposed to the corrosive environment rather than the whole surface of an uncoated structure. The effect of coatings can be demonstrated by comparing the current density of a bare steel pipeline in average soil conditions, which could be up to 30 mA/m^2 , with that achieved on a well-coated and inspected line where a current density of only 0.01 mA/m^2 or even lower may be required to obtain satisfactory cathodic protection. In all cases the current density for protection is based on the superficial area of the whole structure.

Surface area In the case of underground pipelines, calculation of the superficial surface area can be obtained from the diameter and length of line involved. The superficial surface area should include any offtakes and other

Table 10.25 Steps in design of cathodic-protection installation

<i>Sacrificial and impressed-current anodes</i>	
<ol style="list-style-type: none"> 1. Establish soil or water resistivity. 2. Estimate total current requirements which will depend on aggressiveness of the environment, nature of protective coating, area of structure, materials of construction. 3. Establish electrical continuity of structure. 4. Consider requirements for electrical isolation in order to restrict the spread of protective current. Alternatively assess extra current allowance for unrestricted spread. 	
<i>Sacrificial</i>	<i>Impressed current</i>
<ol style="list-style-type: none"> 5. Selected suitable anode metal; calculate total mass of metal for required life. 6. Select individual anode shape to satisfy total current output and current distribution requirements. 7. Check that total anode weight as determined by (6) will satisfy the requirements of (5). 8. Consider facilities for monitoring performance. 	<ol style="list-style-type: none"> 5. Consider the number and disposition of anodes/groundbeds bearing in mind: <ol style="list-style-type: none"> (i) Uniformity of current distribution (ii) Proximity to available power supplies (iii) Avoidance of interaction (iv) Avoidance of mechanical damage (v) Desirability of low resistivity environment. 6. Select suitable anode material 7. Calculate anode/groundbed size, shape, configuration. 8. Calculate circuit resistance and system d.c. volts. 9. Consider facilities required for control/monitoring.

metal structures in electrical contact with the main line. For marine structures the area should include all submerged steel work below full-tide level. In the case of power stations, details of the water boxes, number of passes on coolers and detailed drawings are required. In the case of ships, details of the full underwater submerged area at full load are needed.

Electrical continuity It is essential for any structure to be fully electrically continuous. In the case of pipelines, welded joints are obviously no problem but mechanical joints require bonding. For marine structures individual piles and fendering must be electrically connected either by the reinforcing bars in the concrete deckhead or separately by cable. In power stations and ships, rotating shafts must be bonded into the structure by means of brush gear or a suitable alternative. In the case of modern offshore mooring installations, it may be necessary to install a bonding cable to bring the outerlying dolphins, etc. into the system.

Estimate of current required The surface area of the structure is calculated and the current density required for the particular environment is selected (Table 10.26). In the case of an existing structure the condition of the coating may be unknown and the application of a temporary cathodic-protection system may be necessary to determine the amount of current required for protection, as established by the potential. Such a test to determine the

Table 10.26 Typical values of current requirements for steel free from adverse galvanic influences in various environments

<i>Environment</i>	<i>Current density required for adequate cathodic protection* based on superficial area (mA/m²)</i>
BARE STEEL	
Sterile, neutral soil	4.3–16.1
Well-aerated neutral soil	21.5–32.3
Dry, well-aerated soil	5.4–16.1
Wet soil, moderate/severe conditions	26.9–64.6
Highly acid soil	53.8–161.4
Soil supporting active sulphate-reducing bacteria	451.9
Heated in soil (e.g. hot-water discharge line)	53.8–269.0
Dry concrete	5.4–16.1
Moist concrete	53.8–269.0
Stationary fresh water	53.8
Moving fresh water	53.8–64.6
Fresh water highly turbulent and containing dissolved oxygen	53.8–161.4
Hot water	53.8–161.4
Polluted estuarine water	538.0–1614.0
Sea-water	53.8–269.0
Chemicals, acid or alkaline solution in process tanks	53.8–269.0
Heat-exchanger water boxes with non-ferrous tube plates and tubes	1345.0 overall
WELL-COATED STEELS (e.g. pipelines)	
Soils	0.01

* Higher current densities will be required if galvanic effects (i.e. dissimilar metals in contact) are present.

absolute amount of current required is known as a *current drain* test. Misleading information may, however, be obtained if the results from current drainage tests on bare or coated steel in sea-water are extrapolated, because long-term polarisation effects, together with the formation of a calcareous deposit on the structure, may considerably reduce eventual current requirements. On the other hand, in estuaries and polluted waters special care must be taken to allow for seasonal and other variable factors which may require higher current densities.

Establishing electrolyte resistivity To enable a satisfactory cathodic-protection scheme to be designed, it is necessary to determine the resistivity of the electrolyte (soil or water). This information is necessary to enable the current output of anodes to be determined together with their position and power source voltage, and it also provides an indication of the aggressiveness of the environment; in general the lower the resistivity the more aggressive the environment.

Economics After evaluating these variables, it must then be decided which type of system, i.e. sacrificial anode or impressed current, would be the most economical under the prevailing conditions. For instance, it would obviously be very expensive to install an impressed-current system on only 100 m of fire main. Similarly, it would be equally uneconomic to install a sacrificial-anode

system on hundreds of miles of high-pressure poorly coated gas main. Therefore, each system must be individually calculated taking note of all the factors involved.

Impressed-current Systems

Cathodic-protection schemes utilising the impressed-current method fall into two basic groups, dictated by the anode material:

1. Graphite, silicon-iron and scrap-steel anodes used for buried structures and landward faces of jetties, wharves, etc.
2. Platinised-titanium, platinised-niobium, lead and lead-platinum anodes used for submerged structures, ships and power stations.

These two groups will be discussed briefly since a more detailed account has been given in Section 10.3.

Group 1 Anodes

Scrap steel In some fortunate instances a disused pipeline or other metal structure in close proximity to the project requiring cathodic protection may be used. However, it is essential in cases of scrap steel or iron groundbeds to ensure that the steelwork is completely electrically continuous, and multiple cable connections to various parts of the groundbed must be used to ensure a sufficient life. Preferential corrosion can take place in the vicinity of cable connections resulting in early electrical disconnection, hence the necessity for multiple connections.

Graphite Graphite anodes are usually linseed oil or resin impregnated and supplied in standard lengths, e.g. 2.5 in (approx. 65 mm) dia. \times 4 ft (1.2 m) long and 3 in (75 mm) dia. \times 5 ft (1.5 m) long with a length of cable (called the anode *tail*) fixed in one end. Graphite anodes are still used and were particularly common in early cathodic-protection systems. However, they have tended to be replaced by silicon-iron, the main reasons being (a) graphite

Table 10.27 Impressed-current anodes

Material	Max. working capacity (A/m ²)		Approx. consumption (kg/A year)	
	Soil	Sea water	Soil	Sea water
Scrap steel	5.4	5.4	8.0	10.0
Scrap cast iron	5.4	5.4	6.0	8.0
Silicon-iron	32	32-43	< 0.1	0.1
Graphite	11	21.5	0.25	0.5
Lead	—	107-215	—	—
Lead-platinum	—	1 080	—	—
Platinum	—	< 10 800	—	—
Platinised titanium	—	< 10 800	—	—
Platinised tantalum	—	< 10 800	—	—
Aluminium	—	21.5	—	4.0

tends to spall in use, particularly in chloride environments and (b) its relatively low operating current density ($10\text{--}20\text{ Am}^{-2}$, Table 10.27).

Silicon-iron Silicon-iron anodes are again generally supplied in standard sizes, e.g. 2.0 in (approx. 50 mm) dia. \times 4 ft (1.2 m) long and 3 in (75 mm) \times 5 ft (1.5 m) long and are complete with a cable tail. These anodes are made from cast iron with a high silicon content of 14–15%, together with small percentages of alloying elements such as chromium. The main disadvantage is their extreme brittleness, resulting in transport problems from the foundry to the cathodic protection site, especially if this is overseas.

Group 2 Anodes

This group includes platinised-titanium, platinised-niobium, lead alloys and lead-platinum anodes, which are used for immersed structures, e.g. jetties, sheet piling and power stations.

Platinised titanium These anodes are usually in the form of titanium rod, tube or wire with a coating of platinum 2.5 to 5.0 μm thick. Diameters are generally in the range 3 to 25 mm. In order to reduce the voltage drop in very long anodes, a copper cored variety is available. Platinised titanium anodes may also be used in mesh or plain sheet form and can be fabricated to suit particular applications.

Platinised niobium and tantalum Niobium and tantalum can be used as substrate materials where environmental conditions dictate a higher driving voltage, e.g. brackish water. Use is limited due to relatively high cost. Copper cored materials are again available.

Lead-platinum The alloy is lead together with 0.1–2% silver usually in rod form with platinum microelectrodes inserted every 150 mm. The purpose of these microelectrodes, which take the form of pins, is to stabilise the formation of lead peroxide on the anode surface.

Cathodic Protection of Buried Structures

Soil or Water Resistivity

Soil resistivity measurements are carried out by the Wenner technique using commercially available instruments. Resistivity not only enables the anode resistance and size to be calculated but also indicates the probable corrosivity of the soil or water. In the case of a pipeline route, variations in soil resistivity may stimulate localised corrosion and can cause long line currents; the area in the soil of lower resistivity is usually anodic (more negative) compared to that in the soil of higher resistivity. It is therefore impossible to give any precise ruling as to the rate at which corrosion will occur under any particular soil conditions, and the results of any survey must be taken as giving only a general indication of the probability of corrosion. Chemical

and other forms of industrial contamination of the soil can significantly influence soil resistivities and corrosion characteristics and it is inadvisable to place too much faith in any results where such contamination may have occurred (e.g. in the proximity of chemical plant, etc.).

A typical soil resistivity survey is shown in Fig. 10.22. Soil resistivities will normally indicate whether a cathodic-protection system is advisable in principle and whether impressed current or sacrificial anode schemes in particular are preferable. It may, as a result of the survey, be considered desirable to apply protection to the whole line or to limit protection to certain areas of low soil resistivity or 'hot spots'.

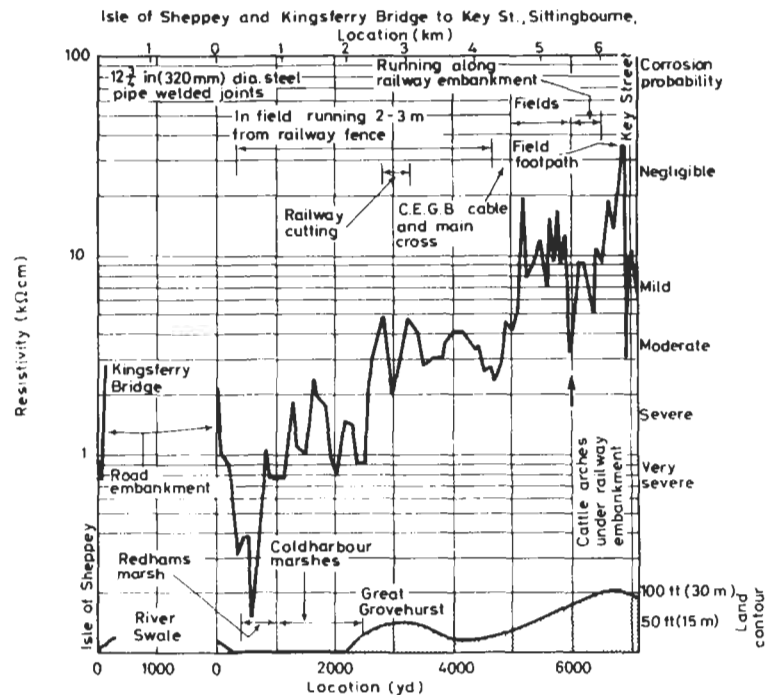


Fig. 10.22 Typical soil resistivity survey

The cost of protecting uncoated structures is relatively high and expense may prohibit complete protection, in which case sacrificial anodes may be installed in the lowest resistivity areas only — on the basis that these are likely to be the most corrosive. In the case of high-pressure gas and oil lines, it is common practice to apply cathodic protection irrespective of the soil resistivity in view of the low cost when associated with modern pipeline coatings and the potential hazards which could occur should even a minute pin hole perforate the pipe. In such cases a soil resistivity survey is only required in the probable areas of groundbeds in order to enable the size of the groundbed, rectifier voltage, etc. to be determined. The soil resistivity also determines the current output of magnesium or zinc anodes should this type of system be preferred (see Section 10.2).

The soil resistivity, measured using the Wenner technique, determines the average soil resistivity to a depth approximately equivalent to the distance between the pin spacings, and it must therefore be recognised that the design figure for groundbed design in a particular location may not be highly precise. At least 10% error in the calculated resistance may be expected.

Soil resistivity surveys are often impractical in built-up areas, but in such areas impressed-current cathodic protection is usually avoided on account of the danger of interaction. Under such conditions adequate protection can be achieved by installing magnesium anodes in the pipe trench should the soil resistivity measurements made when the trench is opened indicate that this is necessary.

Impressed-current Design

Designs can be prepared once soil resistivities and groundbed locations have been determined. Figure 10.23 illustrates typical installations. Design steps are as follows:

1. Select the current density to be applied from the results of cathodic-protection tests and from any available data. On pipeline structures attenuation is always a factor and the average current density is determined from the attenuation curves, or the total current to give protection at the points most distant from the drainage point may be computed.

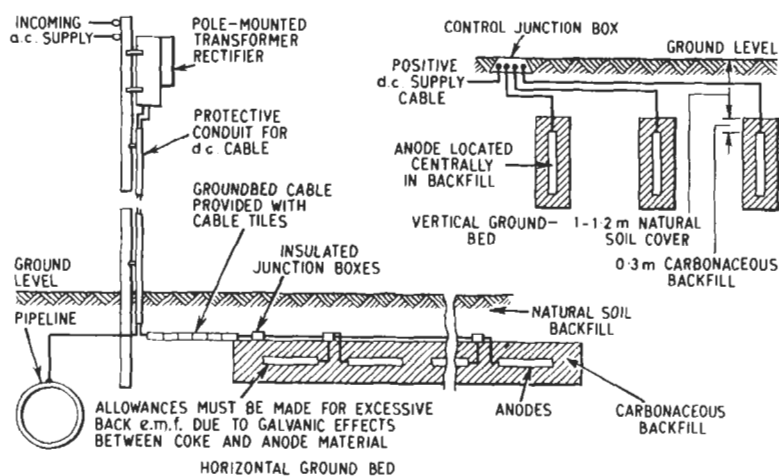


Fig. 10.23 Groundbeds for buried pipes using impressed current

2. Compute the total current requirement to achieve the required current density (total current = current density \times superficial surface area).
3. Design the groundbed system in accordance with procedures outlined.
4. Design the d.c. wiring system for the most economical cable size in

accordance with standard electrical practices and then calculate the total IR drop in the circuit.

5. Select rectifier voltage and current outputs.
6. Design the electrical circuits, fittings and switchgear in accordance with standard electrical practice.
7. Select the location of cathodic-protection test stations.
8. Prepare project drawings and specifications.

The total circuit resistance of a groundbed installation includes cable resistance, resistance of the anode to the carbonaceous backfill plus resistance to earth of the backfill column itself. In the case of sea-water installations, the anode resistance is between the sea-water and the anode surface only.

Anode Backfill

The carbonaceous backfill surrounding an anode is essential and serves a number of functions, e.g.

1. Being of low resistivity it has the effect of increasing the anode size with resulting reduction in resistance to earth.
2. Most of the current is transmitted to the backfill from the anode by direct contact, so that the greater part of material consumption is on the outer edges of the backfill column, enabling the anodes themselves to have an increased life.

The backfill composition may be of several types varying from coke breeze to man-made graphite particles. A coke breeze backfill consists of high-temperature-fired coke breeze or calcined petroleum coke with not less than 95% dry weight of carbon with a maximum resistivity of $50 \Omega \text{ cm}$ when lightly tamped, dry and prior to the addition of lime. A typical specification requires that 100% will pass through a 16 mm aperture, 90% will pass through an 8 mm aperture and not more than 15% will pass through a 1 mm aperture, and that the coke breeze should be thoroughly mixed with 5% by weight of slaked lime.

Resistance of Groundbeds

The resistance of groundbeds for protection of pipelines or anodes for protection of jetties or other sea-water structures, is usually calculated in accordance with the formulae originally developed by Dwight. However, the following abridged formulae are normally used and are sufficient for all practical purposes:

$$\text{Resistance of a single horizontal rod anode } R_H = \frac{P}{2\pi L} \left(\ln \frac{4L}{d} - 1 \right)$$

and

$$\text{Resistance of a single vertical rod anode } R_v = \frac{P}{2\pi L} \left(\ln \frac{8L}{d} - 1 \right)$$

where R_H is the resistance of a single horizontal anode (Ω), R_v is the resistance of a single vertical anode (Ω), P is the resistivity ($\Omega \text{ cm}$) of soil or backfill, L is the length of rod (cm) and d is the diameter of the rod (cm).

Where anodes are installed in special backfill, two series resistances are present—anode to backfill and backfill to soil. In practice, and with coke breeze backfill, a single calculation based upon the dimensions of the backfill column and soil resistivity is satisfactory.

Resistances of several anodes in parallel can be calculated by the formula:

$$R = \frac{\rho}{2\pi NL} \left(\ln \frac{8L}{d} - 1 + \frac{2L}{S} \ell_n 0.656N \right)$$

where R = resistance to earth (Ω) of the vertical anodes in parallel, ρ = soil resistivity ($\Omega \text{ cm}$), N = number of anodes in parallel, L = length of anode (cm), d = diameter of anode (cm) and S = anode spacing (cm).

Deep Well Groundbeds

This type of groundbed is illustrated in Fig. 10.24 and is normally employed where the surface soil resistivities are very high, e.g. in desert areas. They have the advantage of taking up little surface area and can be installed, in the case of a pipeline project, in the existing pipeline wayleave. They have the further advantage of minimising interaction on foreign structures. Abandoned oil or water wells can sometimes be used for this purpose. The type of groundbed can be of the design illustrated or alternatively can be assembled on the surface in a steel case and lowered down a suitably drilled hole.

Determining Rectifier Voltage

In determining the rectifier voltage, the following must be taken into consideration:

1. Voltage drop caused by groundbed resistance, as previously explained.
2. Back voltage polarisation between groundbed and pipeline. In the case of both graphite and silicon-iron anodes, an allowance of 2 V is normally used. This back voltage is that which exists between the anodes and the structure in opposition to the applied voltage.
3. Resistance to earth of the pipeline at the groundbed location. This resistance to earth depends on the quality of the pipeline coating. The better the coating the higher the resistance.
4. Resistance of the cable from the pipeline to the power source and from the power source to and along the anodes comprising the groundbed. This cable resistance must be determined from the standard tables supplied by the cable manufacturer.

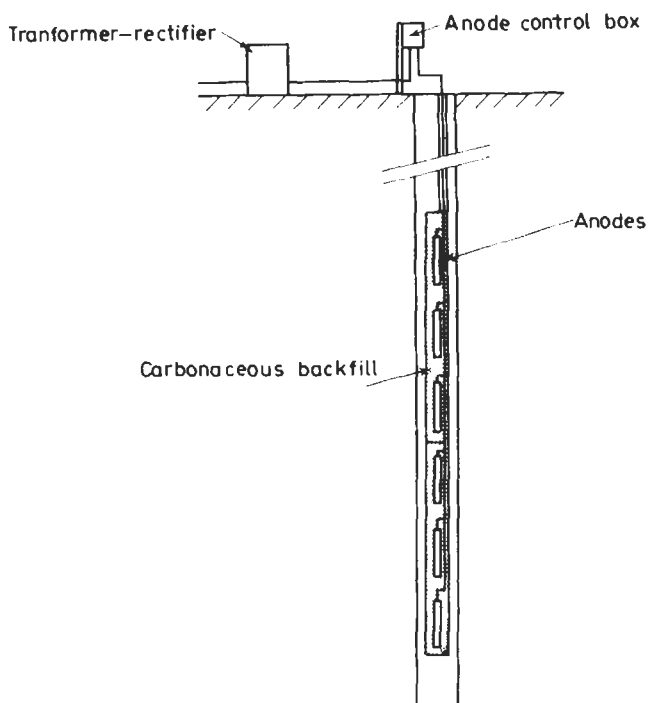


Fig. 10.24 Deep well installation

Once the total circuit resistance is known, applying Ohm's law the rectifier or power-source voltage can be calculated.

Attenuation

When cathodic protection is applied to an underground metal structure the greatest effect on the pipe to soil potential is at the drainage point. This effect decreases, or attenuates, as the distance from the drainage point increases.

Complex structures such as tank farms, tank bottoms and marine installations have complicated attenuation patterns and it is not feasible to use complex equations to determine the effect. This must be determined by a current drain test or by practical experience. For pipelines the attenuation depends on the linear resistance of the pipe, coating resistance, and to some extent the resistivity of the soil. Connections to foreign structures and the method of termination of the line also affect the attenuation (see Section 10.1).

Field Measurements

In order to obtain the actual field attenuation characteristics, a pipeline can be placed under temporary cathodic protection and measurements made

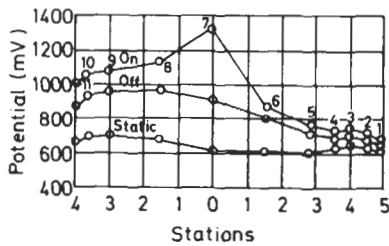


Fig. 10.25 Longitudinal distribution potential on pipeline. Note: 'Stations' refer to points at which the potential is measured

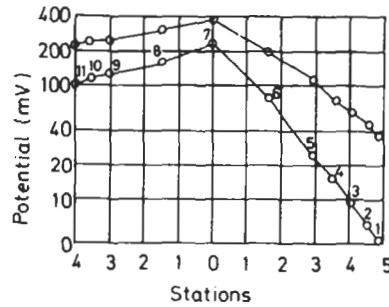


Fig. 10.26 Attenuation curve on pipeline shown in Fig. 10.25. Upper curve shows driving voltage; lower curve the pipe/soil potential

under different cathodic-protection current conditions. A 'natural' pipe to soil potential survey should be made over the length of the line to which cathodic protection is to be applied. These static measurements supply a reference level on which to base the subsequent readings. After the natural survey is completed, measurements are made at the same test points with the temporary cathodic-protection system installed. The pipe to soil potential should be read twice, once with the test current on and once with the current off. The data are then plotted as shown in Fig. 10.25.

The horizontal scale is the distance along the pipeline from the drainage point 0 and the vertical scale is the pipe to soil potential. The polarisation potential and the driving voltage are then plotted on semi-logarithmic paper using the same horizontal scale (Fig. 10.26). Attenuation is more rapid in low resistivity soils than in high resistivity soils. If non-uniform conditions prevail the curves will not plot as straight lines as shown in Fig. 10.26, in which the lines in the left of the figure are typically curved as a result of low resistance.

Measurement Between Drainage Points

The theoretical principles of attenuation have been considered in Section 10.1, but some illustrations are appropriate here. Figure 10.27 shows typical

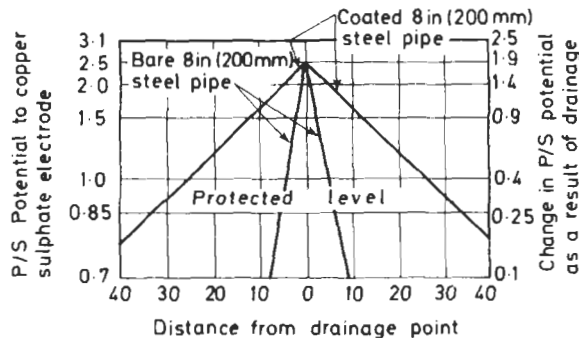


Fig. 10.27 Attenuation curves for bare pipe and poorly coated pipe in similar soils. Note P/S (pipe/soil) potentials will be negative

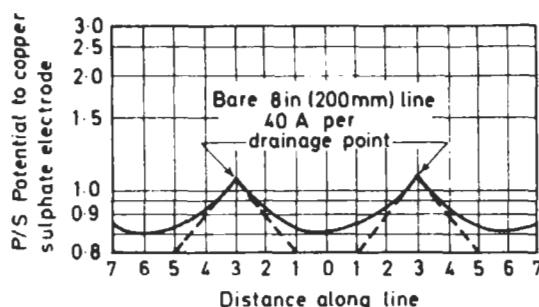


Fig. 10.28 Attenuation curves for multiple drainage points of moderate size

curves for a bare pipe and a poorly coated pipe in similar soils, and it can be seen that the former has a much steeper attenuation curve than the latter. Figure 10.28 shows how the desired protection level of potential has been attained between widely spaced drainage points, in which the dotted curves show the attenuation curves for the individual drainage points.

Coating Resistance

The electrical resistance of a coating on a pipeline will depend upon the effectiveness of its initial application to the metal and on its condition at the time of testing; absorption of moisture may decrease the resistance by as little as 10% during a 2½-year period. The leakage resistance of a given section of pipeline can be determined by the following procedure:

1. Applying temporary cathodic protection to the pipeline and measuring the pipe-to-soil potential for a given driving voltage of various test points spaced along the pipeline from the drainage point. The drainage current should also be measured.
2. Calculating the attenuation constant (see Section 10.1).
3. Measuring or calculating the longitudinal resistance of the pipeline. The resistance can be calculated from

$$R = \frac{2\rho l}{dt}$$

where ρ is the specific resistivity, l is the length of the pipeline, d is the diameter and t is the thickness in appropriate and consistent units.

4. From Section 10.1 calculating R_L the leakage resistance. If it has been evaluated for 1 000 ft of pipeline the leakage resistance of the coating R_c is given by

$$R_c = 262dR_L \quad (10.20)$$

where R_c is in Ω ft and d is the external diameter of the pipe (in).

Types of Cable for Anode Installations

Cables used for anode groundbeds must be well insulated and suited to operational conditions. Mechanical damage from sharp coke particles and chemical attack from generated gases (e.g. chlorine) may be prevented by the use of PTFE additional sleeving or a similar material. Alternatively, chemically resistant cable insulation such as crosslinked polyvinylidene fluoride may be used. This type of cable is essential for deep-well groundbeds where chlorine generation and highly acidic conditions may have to be tolerated.

Power Sources for Cathodic Protection

Where a.c. supplies exist, transformer-rectifiers are the most economical source of d.c. for cathodic protection systems. In the case of pipelines, standard transformer-rectifiers, either oil or air cooled, can be employed. They range in size from 5 A, 5 V for small systems to 100 A, 48 V for major pipeline schemes. A typical output for a well-coated cross-country pipeline in the UK would be 5 A, 48 V. In the case of sea-water jetties where the voltage required is usually low because of the lower sea-water resistivity, a typical rectifier size for a major installation would be 500 A, 18 V. For offshore pipelines and loading platforms where a fire hazard exists, it is usual to employ certified flameproof or intrinsically safe rectifiers to overcome any possibility of fire hazard should faults develop in the unit.

Where a.c. supplies do not exist, other sources of power can be used such as d.c. generators, and either diesel or gas driven. Alternatively, thermo-electric generators may be considered if the power requirement is relatively low. Thermo-electric generators are available in relatively small outputs only as shown in Table 10.28. They have the advantage of being completely self-contained since they are powered by taking off some of the gas which passes through the pipeline.

Table 10.28 Thermo-electric generators

<i>Electrical characteristics</i>				<i>Fuel consumption*</i>		
<i>Power†</i> (W)	<i>Load voltage†</i> (V)	<i>Load current†</i> (A)	<i>Power range‡</i> (W)	<i>Propane</i> (kg/h)	<i>(litre/h)</i>	<i>Natural gas</i> (m ³ /h)
9	1	9.0	8.5–10.0	0.033	0.077	0.035
15	2	7.5	14–18	0.059	0.105	0.054
28	3.8	7.3	26–32	0.082	0.191	0.1
50	6	8.3	46–60	0.136	0.322	0.2
100	12	8.3	92–120	0.272	0.636	0.4
200	6	33	188–240	0.544	1.273	0.8

* Fuel consumption may vary slightly depending upon air shutter adjustment.

† Values are typical at 24°C ambient temperatures, under a fixed matched load at constant gas pressure.

‡ Typical power output range of generator for a variation in ambient temperature from 51.5 to –31.5°C.

Protection of Power Station or Refinery Sea-water-cooled Circulating Water Systems

Sacrificial Anodes

The use of sacrificial anodes in circulating water systems is limited to the application of cathodic protection to stop gates, coarse screens and other plant that are readily accessible so that the anodes can be replaced when they are consumed. Such anodes are not normally used in condensers, pumps and auxiliary coolers for the following reasons:

1. Frequent replacement required with consequent shut-down of the plant concerned.
2. Anodes required to be very large to provide the current density necessary, and with a reasonable life. Anodes can interfere with the water flow.
3. Corrosion products from anodes can cause tube blockage and subsequent failure.

Impressed-current Anodes

Anodes for the internal protection of plant are normally of platinised titanium.

Continuous Anodes Consist of considerable lengths of relatively flexible copper-cored material which can be contoured to suit restricted spaces or to distribute current in a localised fashion. Typically they may be used in water boxes at a non-ferrous tubeplate/ferrous water box junction. Anode terminations pass through the water box via insulating entry points and the anodes are supported on insulators within the box. Anode/cathode distance must be such as to prevent the anode becoming engulfed in calcareous deposit that forms on the cathode.

Rod Anodes These consist of solid or copper-cored titanium rod, portions of which can be platinised. They range from 6 to 25 mm in diameter and are normally supplied pre-assembled in a steel or unplasticised p.v.c. mount ready for screwing into prepared bosses on the plant under protection. Electrical connections are made via cables in the usual way. The anodes are spaced to give even current distribution.

Tubular Anodes Tubular anodes are supplied in diameters between 12.5 and 32 mm and have been designed for installations where water conditions on the plant under protection are known to be turbulent. The tubular anode has a number of holes drilled in the active portion of the anode and the non-active portion is filled with sand to act as a damping agent. As in the case of rod anodes they are supplied complete with mounts ready for installation in the prepared bosses on the plant under protection. They are particularly suitable for internal protection of pump casings and internal protection of pipelines, carrying salt water or other low resistivity liquids.

Impressed-current Systems

Impressed-current systems for power stations are somewhat more sophisticated than those required for pipelines or marine structures inasmuch that a large number of items of plant, with a wide range of current requirements, are protected by one transformer-rectifier. Each section of every water box in order to provide even current distribution requires one or more anodes. In the case of a large circulating water pump as many as 30 anodes may be required to provide the current distribution necessary. Three types of system should be considered as follows:

1. Manually controlled.
2. Automatically thyristor controlled.
3. Automatically controlled modular.

Manually Controlled System A manually controlled system comprises one or more transformer-rectifiers each with its associated control panels which supply the d.c. to the various anodes installed in the water box spaces. Each transformer-rectifier is provided with its own control panel where each anode is provided with a fuse, shunt and variable resistor. These enable the current to each anode to be adjusted as required. Reference cells should be provided in order to monitor the cathodic protection system. In the case of a major power station, one transformer-rectifier and associated control panel should be provided for separate protection of screens, circulating water pumps and for each main condenser and associated equipment.

When coolers or condensers are shut-down but remain full of water, the amount of current required to maintain satisfactory cathodic protection is considerably reduced. If the current is not reduced over-protection occurs and excessive amounts of chlorine can be generated which would tend to accumulate in the upper section of the water boxes causing considerable corrosion, not only to the water boxes, but also possibly to the tubes. To ensure against this a stand-by condition should be included on the control panel which effectively reduces the current required under shut-down conditions. This control is effected by a limit switch fitted to the outlet valve of the condenser or cooler concerned. It is impossible to determine exact requirements for the protection of circulating water systems in advance and it is normal to adjust the current to provide protection during commissioning.

Automatically-thyristor-controlled System This method is basically the same as the manual system. However, the current output of the transformer-rectifier is automatically maintained at a level to ensure satisfactory cathodic protection under all operating conditions. This is achieved by means of sensing electrodes located in the main item of plant, e.g. main condenser, which feeds back signals to an automatic control device within the transformer-rectifier. The control device is pre-set at the required potential and any incoming signals are compared with this pre-set potential and the level of current either raised or lowered until the incoming signal agrees with that of the pre-set potential in the automatic device.

It is also usual to fit reference (monitoring) electrodes as an independent check on the performance of sensing electrodes.

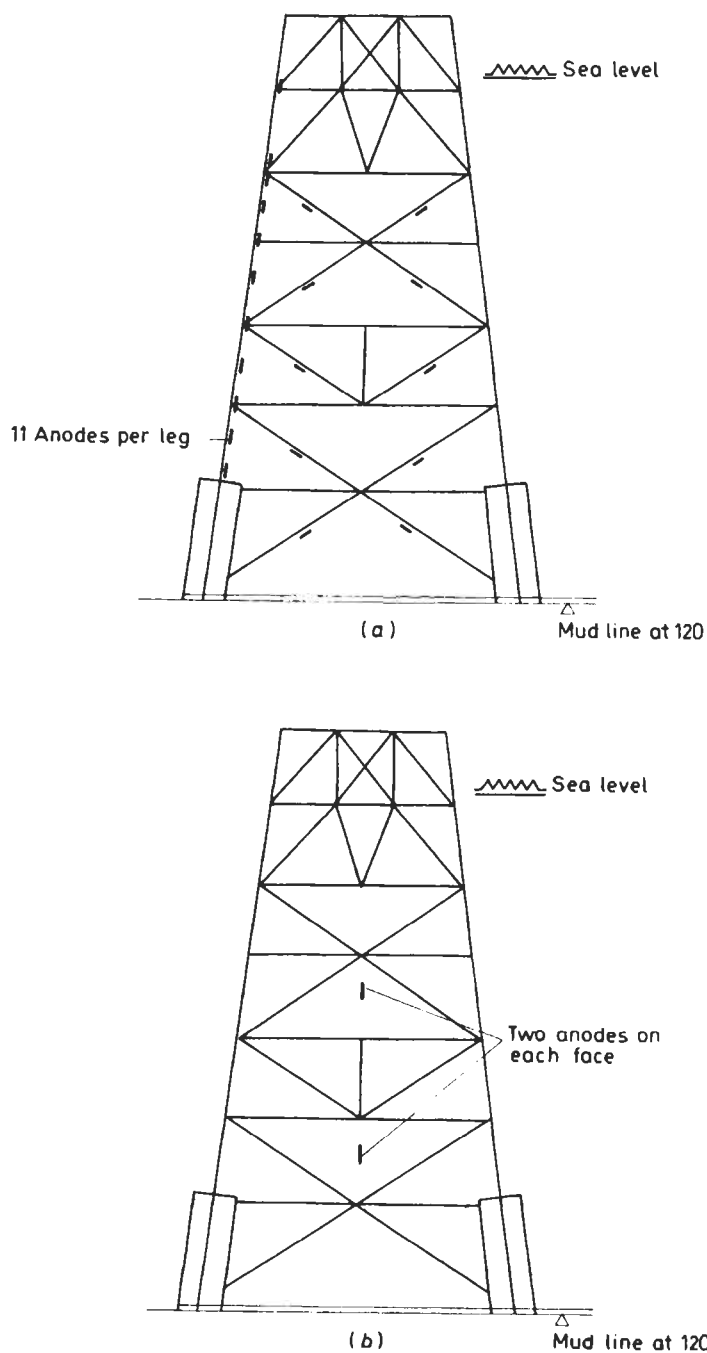


Fig. 10.29 Protection of offshore marine oil-drilling rig. (a) With external zinc (or aluminium) anodes and (b) with impressed current using platinised titanium or platinised niobium. (Compare the large number of anodes used in (a) with the small number used in (b))

Automatically Controlled Modular System This method employs one large manually controlled transformer-rectifier used in conjunction with a number of modular cabinets located adjacent to each item of plant requiring protection. The main transformer-rectifier feeds d.c. to each of the module units and the modular unit provides the exact amount of current required by the item of plant in question.

Marine Structures

The method of applying cathodic protection to immersed structures will depend on several factors including:

1. Size of the project.
2. Availability of power supply.
3. Possibility of problems from interaction.
4. Necessity for safety from spark hazard.
5. Expected economic life of the system.

Figures 10.29*a* and *b* give an indication of the relative numbers of anodes that may be involved for sacrificial anode and impressed-current systems.

Current density requirements depend on the environment, galvanic effects, velocities and other factors influencing polarisation. In the absence of galvanic influences or other secondary effects 30 mA/m^2 may be sufficient in sea-water to maintain adequate polarisation for protection once it has been achieved; it is however normally necessary to apply $100\text{--}150 \text{ mA/m}^2$ to achieve initial polarisation within a reasonable period and if rapid protection is required, current densities as high as 500 mA/m^2 may be applied.

Groundbeds remote from the structure can be considered but usually with this type of installation problems arise due to damage to the connecting cable by ships' anchors, etc. The calculation of rectifier voltage/anode resistance is exactly as described for impressed current pipeline installations except that the voltage required is very small because of the low resistance of the electrolyte—normally $20\text{--}36 \Omega \text{ cm}$ for typical sea-water.

For protection of sheet-steel piling, the anodes are normally mounted within the re-entrants of the piles to prevent mechanical damage by berthing ships, dredging, etc. (Fig. 10.30).

As in the case of power stations, where there is known to be considerable variation in operating conditions due to tidal changes, or in estuary waters variations in salinity, automatic control systems may be desirable. For such systems the current output of the transformer-rectifier is controlled by thyristor or transducers. Sensing electrodes are permanently installed on selected piles and transmit the electrode potential of the steel back to the controlling device. This type of system enables the most economic amount of current to be provided under all operating conditions.

Ships

Cathodic protection is effectively supplied to ships' hulls and also to the tanks of oil tankers and other vessels where sea-water is used for ballast or other

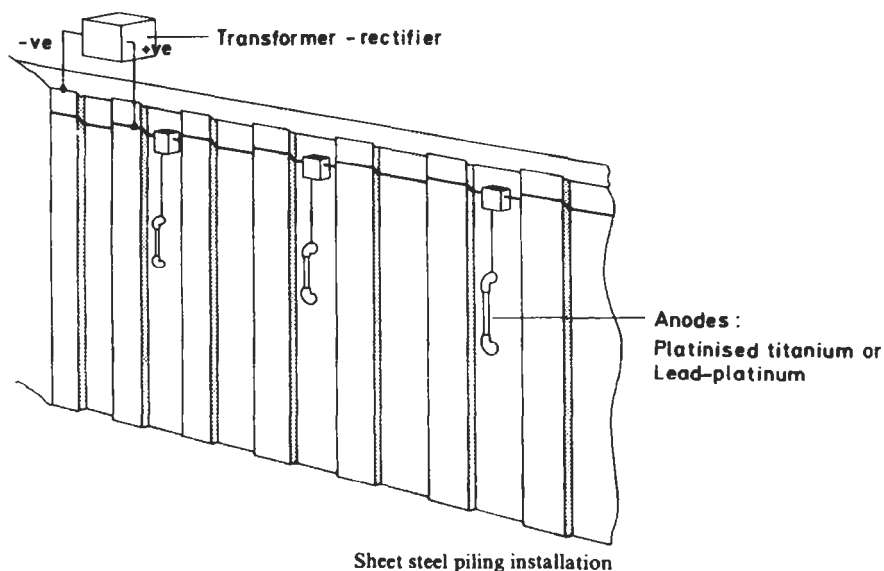


Fig. 10.30 Sheet steel piling installation

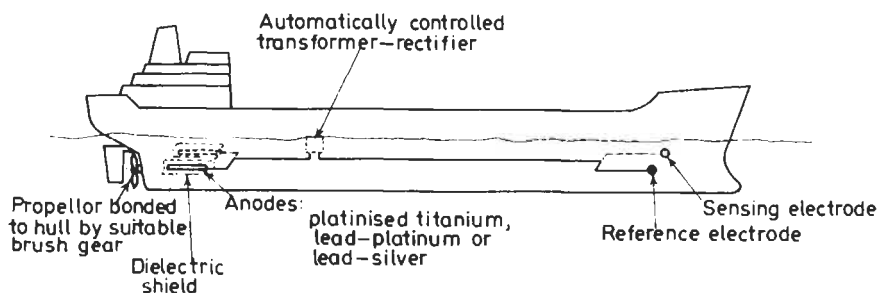


Fig. 10.31 Impressed-current system for ships

purposes. For internal protection sacrificial anodes are normally employed of the zinc or aluminium type. Impressed current is not normally used because of the potential fire hazard and also because of the anodic generation of chlorine inside closed water spaces. External hulls can be protected either by sacrificial or impressed-current methods, although impressed current is now preferred (Fig. 10.31). Anodes of platinised titanium, lead-platinum or lead, are mounted on the hull below the water line and can be designed to have current outputs of up to 200 A. In vessels such as tankers, where there may be access problems, the anodes are located either at the stern or the forward end of the ship. All cable or other entries through the hull plate must be carefully designed using a special backing plate and the complete system has to be submitted to the Ship Approval Authorities prior to installation. Because of the rapid variation in conditions, the condition of the paint surface, etc. all schemes for ships are automatically controlled.

The transformer-rectifiers are either thyristor or transductor controlled and operate in a similar manner to that described for power stations.

Water Storage Tanks

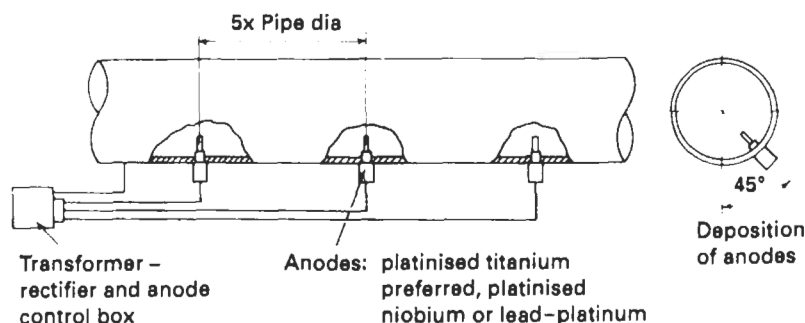
Sacrificial anodes are of limited application due to accumulation of anode corrosion product and also in many cases, to high water resistivity.

Impressed current systems are normally based upon anodes of silicon iron, platinised titanium or platinised niobium. The method of anode installation is usually by suspension. The anode configuration and number must be such as to ensure uniform current distribution. Considerable use is made of wire-type platinised-titanium, and niobium anodes which offer minimal weight and relative ease of mounting/suspension.

Coatings are normally employed for water storage tanks which result in relatively low total current requirements in association with the current densities given in Table 10.26.

Internal Protection of Pipelines

The current spread from an internally immersed anode is directly related to pipe size and the resistivity and temperature of the water; with sea-water having a resistivity of about $30 \Omega \text{ cm}$, anodes are normally required on a 10 in (250 mm) pipe at about 1 m centres and in the case of a 30 in (760 mm) pipe, at 3 m (10 ft) centres (Fig. 10.32). Small bore or high resistivities and velocities further reduce the anode spacing.



Typical current density (sea-water) = 200 mA/m^2

Fig. 10.32 Internal protection of pipeline

Cathodic protection is therefore normally practicable only in large bore pipes carrying salt water. Under special circumstances, however, it has been found necessary to use cathodic protection in fresh water and in these instances anodes have been run longitudinally down the entire length of the pipe, but the cost of such schemes is usually prohibitive.

Economics

Cathodic protection design involves achieving an economic balance between installation costs, maintenance costs, initial cost of power units and power consumption. Because both the cost of the rectifier and the cost of the electric power consumed are contingent on the operating voltage of the system, it is desirable to keep the operating voltage as low as possible; for this reason a low resistance groundbed is desirable when it is economically feasible. Typical cost curves plotted on a cost versus the number of anodes in a groundbed for an assumed set of conditions are shown in Figs. 10.33 and 10.34. Figure 10.33 is based on installed costs only, whereas Fig. 10.34 is the minimum annual cost.

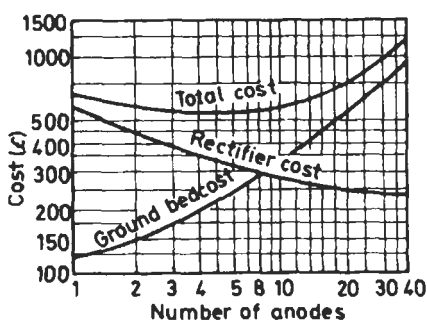


Fig. 10.33 Total cost in relation to number of anodes installed

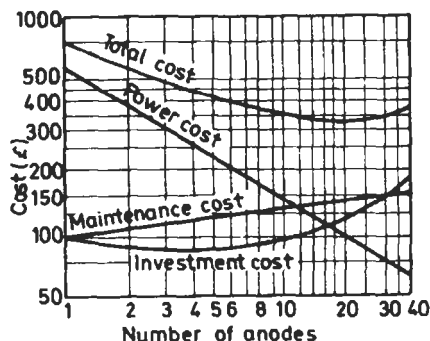


Fig. 10.34 Variation of minimum annual cost with number of anodes installed

Recent Developments

Sacrificial Anode Systems (see also Section 10.2)

As the general standard of protective coatings has improved (materials, application and construction standards) the use of sacrificial anodes has extended to soil of ca. 10 000 ohm cm or more for buried pipelines. By using anodes in extruded 'ribbon' form and placing them as close as possible to the structure to be protected they can be used in soils of high resistivity.

Impressed-current Anodes (see also Section 10.3)

Mixed Metal Oxide Coated Titanium As an alternative to platinised titanium, these materials are finding increasing use in seawater and soil based deep well groundbed applications.

Silicon-iron and Graphite Anodes of these materials are now frequently manufactured with the anode cable tail connected at the centre of the rod

length in order to minimise preferential corrosion. This is particularly the case for silicon-iron anodes which can be readily cast in a tubular form to minimise mass.

Magnetite Anodes of cast magnetite are now available. The anodes are produced as a hollow cylinder closed at one end (typically 60 mm diameter \times 720 mm length). The method of cable connection is relatively difficult and requires the inner surface of the casting to be copper plated. At a current density of 75 A m^{-2} , consumption rates in seawater of less than 1.5 g/Ay are claimed.

Conductive Polymers Anodes currently available consist of a conductive-polymer graphite material coated on to a multistrand copper conductor. The polymer provides an active surface but shields the conductor from chemical attack. A non-conductive outer braid may be used to give abrasion resistance and avoid direct contact with the cathode. The finished anode has the appearance of an electric cable and is claimed to have applications for buried/immersed structures and for internal protection of tanks, etc. Anode current densities are typically given as $14\text{--}30 \text{ mA m}^{-2}$.

Power Sources for Cathodic Protection

Solar Power With improved technology and production methods considerable use is being made of solar power in remote locations. The output of photovoltaic arrays is used to maintain conventional storage batteries in a state of charge. The cathodic protection system is in turn energised from the batteries. It is usual to incorporate sufficient battery storage to accommodate a number of 'no-sun' days. Whilst in theory the capacity of equipment is unlimited, a practical maximum would be ca. 500 W.

Turbo-alternators These find an application in pipeline cathodic protection systems, particularly where the liquid or gaseous product in the pipeline can be used as a fuel. The turbo-alternator is usually supplied as part of a complete and fully assembled package incorporating fuel pressure controls, filters, a.c./d.c. conversion and d.c. output controls. System capacity would typically fall within the range 200–3000 W.

Conclusion

Although the principles of cathodic protection are essentially simple and were in fact first outlined by Sir Humphry Davy in 1824, the application of the method to practical problems remains more of an art than a science. A properly designed cathodic protection system will be both economical and effective. On the other hand an incorrectly designed scheme will be inefficient, uneconomical and under certain circumstances may accelerate corrosion instead of controlling it.

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10.5 Stray-current Corrosion

If a continuous metallic structure is immersed in an electrolyte, e.g. placed in the sea or sea-bed or buried in the soil, stray direct currents from nearby electric installations of which parts are not insulated from the soil may flow to and from the structure. At points where the stray current enters the immersed structure the potential will be lowered and electrical protection (cathodic protection) or partial electrical protection will occur. At points where the stray current leaves the immersed structure the potential will become more positive and corrosion may occur with serious consequences.

In practice, corrosion of buried metallic pipes or cable sheaths is liable to occur when direct current flows from equipment associated with electric railway traction systems, trolley vehicle or tramway systems, electricity supply systems and electric welding or similar equipment in factories or ship-yards. This type of attack is known as *stray-current electrolysis* and is particularly severe in the vicinity of traction systems running on rails in direct contact with the soil or when earth leakage faults develop on d.c. power supply systems. Small signalling currents may be detected flowing to or from buildings housing telecommunications or signalling apparatus and stray galvanic or earth currents may also flow from earth systems associated with protective or signalling equipment.

Stray-current electrolysis occurring as a result of the application of cathodic protection to a nearby immersed or buried structure is known as *cathodic-protection interaction* and is described in Section 10.6.

The corrosion of underground pipes and cables caused by the electrolytic action of stray currents from d.c. electric railway and tramway systems has long been a serious problem. Regulations limiting the maximum potential between tramway rails and neighbouring buried structures and the maximum potential difference between points on the rail systems have been in operation in the UK since 1894 and in Germany since 1910¹.

In 1929, an international commission, the *Commission Mixte Internationale pour les expériences relatives à la protection des lignes de télécommunication et des canalisations souterraines* (C.M.I.), was enlarged and its scope extended for the purpose of making experimental studies concerning the corrosion of pipes and cables. The C.M.I. membership was composed of international technical experts from learned bodies, research laboratories and manufacturers of electrical equipment, and representatives of authori-

ties responsible for electric power supply, electric railways, electric tramways, gas supply, and telecommunications.

Members of the C.M.I. co-operated with the *Comité Consultatif International Téléphonique et Télégraphique* (C.C.I.T.T.) to produce recommendations² for the protection of underground cables against the action of stray currents arising from electric traction systems. These recommendations are revised at regular intervals and, although they specifically refer to the protection of telephone cables, most of the preventive measures and testing methods are also applicable to pipe systems.

In the USA, interest has been particularly concentrated on leakage currents from inter-urban and street railway tracks, and the 1921 Report of the American Committee on Electrolysis³ summarises the problem and the methods of controlling electrolytic corrosion applied both in America and in many European countries.

Mechanism of d.c. Stray-current Corrosion

An electric railway or tramway system with an adjacent buried pipeline or cable which may cross the running rails at intervals is illustrated in Fig. 10.35 in which the arrows indicate the general flow of stray currents when one vehicle is in service. Rapid variations of current and potentials will occur as the tram or train moves along the rails. Corrosion will occur at points near the sub-station or near negative feeders where the stray current leaves the buried structure to return to the negative busbar at the sub-station.

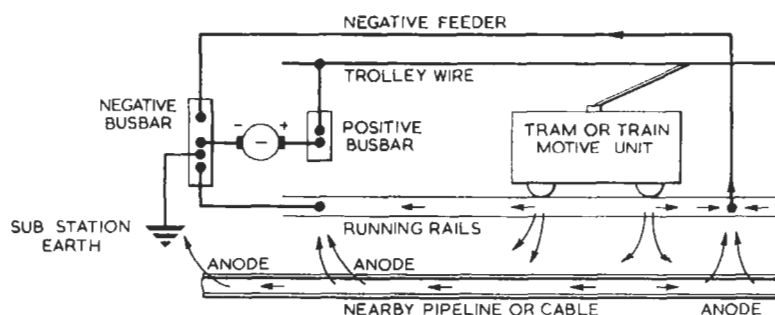


Fig. 10.35 Stray current from d.c. traction system

Damage is greatest with the 'Third Rail System' illustrated in the figure, since the negative pole of the generator is connected to the running rails which are not deliberately insulated from the surrounding soil, and in some instances cables and pipes have been severely pitted by stray-current corrosion in less than one year after installation. Some d.c. electric railways operate on the 'Fourth Rail System' in which the current is collected from specially insulated positive and negative conductor rails which are not in electrical contact with the running rails or the surrounding soil.

When the motive unit is taking current from a third rail system the potential of the rails immediately beneath the wheels of a tram or train may rise

10 or more volts above normal rail potential. Since the joint resistance to earth of the running rails will usually be less than $1\ \Omega$ there will be fluctuating potential changes in the surrounding soil, and tests in these circumstances have shown that the potential difference between two reference electrodes placed in the soil a hundred metres or so apart near the rails will vary rapidly in amplitude and polarity and may reach peak values of 3 or 4 V.

Most investigators agree that the electrolytic effects attributable to the operation of a d.c. traction system depend on the net amount of current per unit area passing from pipe or cable into the adjacent soil. The most common method of assessing the order of magnitude of this current density is measurement of the change in potential to nearby earth by means of a high-resistance recording voltmeter connected between the buried structure and a reference electrode [$\text{Cu}/\text{CuSO}_4(\text{sat.})$] buried in the soil close to the structure. The natural structure/soil potential (the 'shut-down potential') is ascertained by recording the steady potential attained after the system has been de-energised for at least an hour.

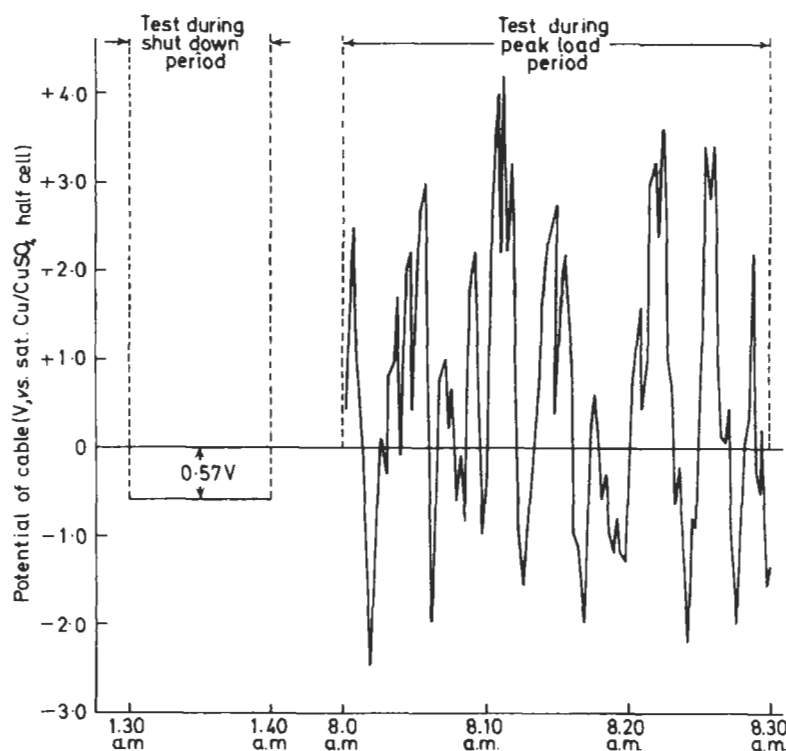


Fig. 10.36 Variation of cable sheath potential due to stray d.c. traction currents

The variation in potential between the sheath of a lead-covered cable lying parallel to a d.c. railway system and a reference electrode placed close to the cable is shown in Fig. 10.36. The shut-down potential of the cable in this test was -570 mV [$\text{Cu}/\text{CuSO}_4(\text{sat.})$]. There is a marked positive change in

mean cable sheath potential during the period 8.0 a.m. to 8.30 a.m. and similar but smaller potential changes were measured at off-peak periods.

a.c. Stray-current Corrosion

In nearly all known cases of stray-current corrosion the damage is caused by direct currents, but leakages of alternating currents at industrial frequencies have been suspected of causing corrosion of buried metallic structures. The mechanism of corrosion caused by a.c. is not clearly understood and fresh studies are being made⁴. However, the corrosion caused is much less severe than with stray d.c. and experiments⁵ indicate that stray a.c. at 50 Hz will produce less than 1% of the corrosion caused on most buried metals by an equivalent d.c.

Methods of Control

The C.C.I.T.T. have recommended that the amount of stray current from the running rails should be controlled by limiting the average difference in potential between any point on the running rails and the nearest sub-station negative feeder bus-bar. The average difference in potential is defined as the average potential over all working days, each day counting as 24 h, whatever the effective period of service each day may be.

The amount of corrosion damage resulting from the operation of d.c. railways is generally less than the corrosion caused by street tramway systems since the railway track insulation is better, the frequency of service is less, and pipes and cables are usually buried further from the running rails.

A brief summary of the effects of stray currents from d.c. traction systems on buried structures is given by Evans⁶ who describes methods by which the damage may be diminished. When corrosion occurs at points where the stray current from a d.c. electric railway or tramway leaves the buried structure to return to the traction system, attention should first be given to reducing the amount of stray current by improving the conductivity of the running rails and by regular rail-bond testing. Consideration should also be given to the provision of additional negative feeders and to increasing the resistance to earth of the running rails whenever possible, e.g. by improving drainage, embedding rails in bituminous material, etc.

In addition to these precautions, the most satisfactory way of preventing corrosion on nearby buried structures is by means of drainage bonds. The structure to be protected is made cathodic to the surrounding earth by being connected to the negative feeders or to suitable points on the running rails. The connection may be direct, through a resistance or similar current-controlling device, or through a suitable rectifying device (polarised electric drainage). The rectifier must be capable of passing a current of about 1 A from the buried structure to the negative feed of the traction system when the voltage of the structure rises by about a quarter of a volt above the potential of the adjacent rails. The rectifier must also be able to carry currents in excess of 50 A without breakdown.

Telephone cable sheaths have been successfully protected by this method, using germanium or silicon rectifier elements connected at intervals between the sheaths and the adjacent tramway rails. In a recent project a steam-operated railway system was electrified using 660 V d.c. Before electrification the potential of an adjacent lead-sheathed cable was steady and measured -470 mV [$\text{Cu}/\text{CuSO}_4(\text{sat.})$] as shown in Test 1 of Fig. 10.37. After electrification of the railway system positive and negative fluctuations of potential were measured on the cable sheath and there was a general shift of potential towards values more positive than the steady potential of -470 mV , as shown in Test 2 on the graph. Test 3 shows that a drainage bond containing a silicon rectifier element connected between the running rails and the cable sheath ensured that the sheath remained cathodic to the surrounding soil.

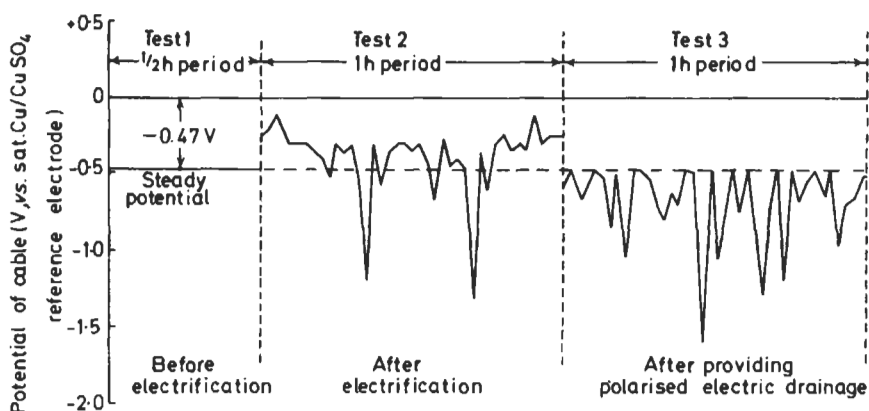


Fig. 10.37 Improvement effected by the provision of polarised electric drainage

A substantial reduction in the amount of stray current picked up by nearby buried pipes or cables may be achieved by interrupting the longitudinal conductivity of the structure by means of insulating gaps or joints. Care must be taken in siting the gaps, and they should preferably be placed in localities where the current tends to enter the structure and at points on each side of the track where the pipe or cable crosses under the rails.

Protection may also be obtained by insulating structures from the soil by means of protective coatings. Pipes may be dipped in bituminous compounds and wrapped with hessian, glass-fibre, or similar materials.

Cable sheaths may be covered with paper and hessian wrappings impregnated with bituminous compounds or with extruded or taped plastics outer sheaths. At pinholes or discontinuities in protective coatings the sheath will be particularly liable to electrolytic corrosion in stray-current areas, and it is desirable to supplement this form of protection by drainage bonds or direct cathodic protection.

Calculation of the amount of stray current entering or leaving a buried structure is a difficult matter, and a solution is usually possible only if the layout of the buried plant is simple. The very complicated cases normally met with in practice are not usually capable of solution, owing to hetero-

geneity of the soil, difference in pipe coatings, variable-resistances between pipe joints, and variation in spacing between buried pipes or cables. Estimates of the potential changes on structures due to nearby traction systems are particularly difficult because of wide and rapid fluctuations in track potentials caused by movement of vehicles and by variable loads on motive units.

Electric Traction Systems

The foregoing paragraphs refer particularly to stray d.c. from railways, tramways, trolley vehicles, mobile cranes and similar systems where the running rails or metallic supports are in direct contact with the earth. Underground d.c. tube railways usually operate on the fourth rail system and may be enclosed within cast-iron tube linings so that there is little or no stray current.

In recent years there has been a tendency to use a.c. in preference to d.c. for industrial purposes, but d.c. systems may still be operating in shipyards, steelworks and similar sites for motive power and also for mobile cranes, lighting and control equipment. The running rails and mountings of such systems are usually in close contact with the earth and severe leakages can be expected to occur, either accidentally or as a result of deterioration with age.

Particular care should be taken when installing metallic pipes or cables in the vicinity of third rail d.c. traction systems. Electrical separation can best be improved by the use of insulating coverings in the form of epoxy resin coatings, extruded plastic sheathing or wrapping tapes with a sealing compound. The use of insulating gaps has already been referred to but this method, although cheaper, is usually less effective.

Rail continuity bonds and negative feeders should be regularly inspected and tested, and the insulation to earth of the third rail or overhead catenary wires and the running (return) rails maintained satisfactorily. Track maintenance should include the renewal of sleepers and rail bedding material if necessary.

In most cases the potential of the running rails to earth will fluctuate rapidly from the normal shut-down potential, and the use of polarised drainage bonds connected between the running rails and nearby buried plant can be most effective. Such bonds, together with the associated rectifiers, must be of low resistance and capable of handling large surges of current from structure to rail or to a negative feeder.

The effectiveness of the various protective measures adopted should be assessed by making shut-down tests and comparing the results with tests made during peak-load periods (see Fig. 10.36).

Catastrophic corrosion damage to buried structures may occasionally occur as a result of earth leakage faults on d.c. equipment or on traction systems using metallic posts to support overhead catenary wires. Care should be taken when making earth potential measurements because of the high potential gradients that may be present.

Submarine Cables

Intercontinental, inter-island or similar sea and river crossings of d.c. power supply and telecommunications submarine cables may use earth return in order to reduce the loop resistance of the power feeding path and to save copper.

The connection with earth is made using earth electrodes at or near the terminal ends. The electrodes may be immersed in the sea or buried on land and, at one end of the system, the electrode will be negative to the surrounding earth. Part of the return current may therefore flow via nearby buried or immersed pipes and cables.

Submarine telecommunications cables operate at less than 1 A, but submarine power cables may operate at several hundreds of amperes and will require larger spacing between the earth electrodes and nearby buried or immersed structures. If possible, tests should be made with trial earth electrodes at both ends of the submarine cable and on-off tests made before bringing the power supply on the system into permanent use.

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10.6 Cathodic-protection Interaction

Stray currents are produced in the electrolyte during the operation of cathodic-protection systems and part of the protection current may traverse nearby immersed structures which are not being cathodically protected. The resultant corrosion produced on the unprotected structure is referred to as *corrosion interaction or corrosion interference*.

The cathodically protected primary structures may be the hulls of ships, jetties, pipes, etc. immersed in water, or pipes, cables, tanks, etc. buried in the soil. The nearby unprotected secondary structures subjected to interaction may be the hulls of adjacent ships, unbonded parts of a ship's hull such as the propeller blades, or pipes and cables laid close to the primary structure or to the cathodic-protection anode system or groundbed.

The lines of flow of the protection current and the interaction current when cathodic protection is applied to a pipeline buried in the soil parallel to a buried secondary pipeline, are shown in Fig. 10.38. The distribution of

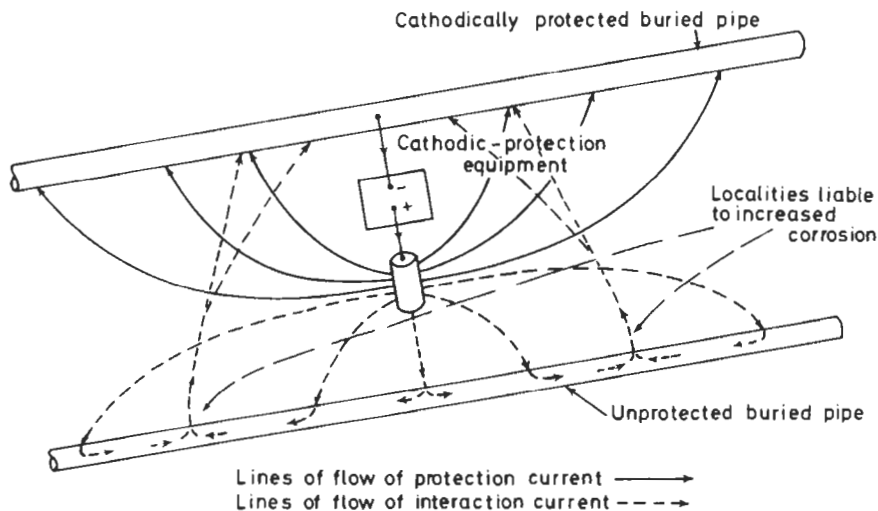


Fig. 10.38 Cathodic protection and interaction currents with parallel pipelines. Note that the pick-up area is the point on the unprotected pipe nearest to the groundbed; at this point the current flows in opposite directions and attains a maximum at the points of discharge

potentials along the two pipelines broadly follows the exponential distribution described in Section 10.1.

Methods of Estimating Interaction

Methods of estimating the amount of interaction between parallel buried pipeline systems have been described by Sunde¹ and Pope². In practice the calculated changes in potential are distorted because of variations in spacing between the structures, changes in soil resistivity and lack of uniformity of the pipe coatings. Two sources of interaction are considered, (a) that caused by current flowing from the groundbed (the *anode* effect) and (b) that caused by the protection current flowing to and from unprotected buried structures in the vicinity (the *structure* effect). The net effect at any point on the unprotected structure will be the sum of the anode and structure effects.

Current due to the anode effect The potential of the earth near the groundbed of a cathodic-protection system becomes more positive as the groundbed is approached (see Fig. 10.7, p. 10:10). A structure buried near the groundbed will pick up current due to this variation in the soil potential and current will flow in the structure in each direction away from a point close to the groundbed (Fig. 10.39). The upper curve AGA' in Fig. 10.39 shows how the current in the unprotected structure changes owing to the anode effect.

Current due to the structure effect Due to leakage of the protection current through the soil between the protected structure and nearby unprotected structures, part of the protection current may flow in an unprotected structure in a direction towards the point of connection to the cathodic-protection equipment. The change in current in the unprotected structure due to this effect is indicated by curve SGS' in Fig. 10.39.

The relative amplitude of the two curves will depend on the attenuation constant of the protected and unprotected structures, the spacing between them, and the distance between the two structures and the groundbed. The total effect at any point on the unprotected structure is obtained by adding together the two currents due to (a) and (b) as shown in curve NGN' .

The rate at which the net current is picked up or discharged will be proportional to the change in structure/soil potential along the unprotected structure and this is shown by the dotted curve $PCG'C'P'$ in Fig. 10.39. At points where current is picked up the potential change is negative and the natural rate of corrosion is reduced as shown by the dotted curve below XX' . The structure/soil potential is made more positive where the interaction current is discharged and the rate of corrosion at such points is increased, as shown by the dotted curve above XX' . The maximum positive structure/soil potential occurs where the gradient of the net current curve NGN' is steepest, that is at points C and C' on the potential curve $PCG'C'P'$.

If, with impressed-current protection, the groundbed is installed near the unprotected structure, large negative changes may occur on the structure at points close to the anode. The maximum positive potential change is usually found on the unprotected installation at a distance of 270–450 m from the

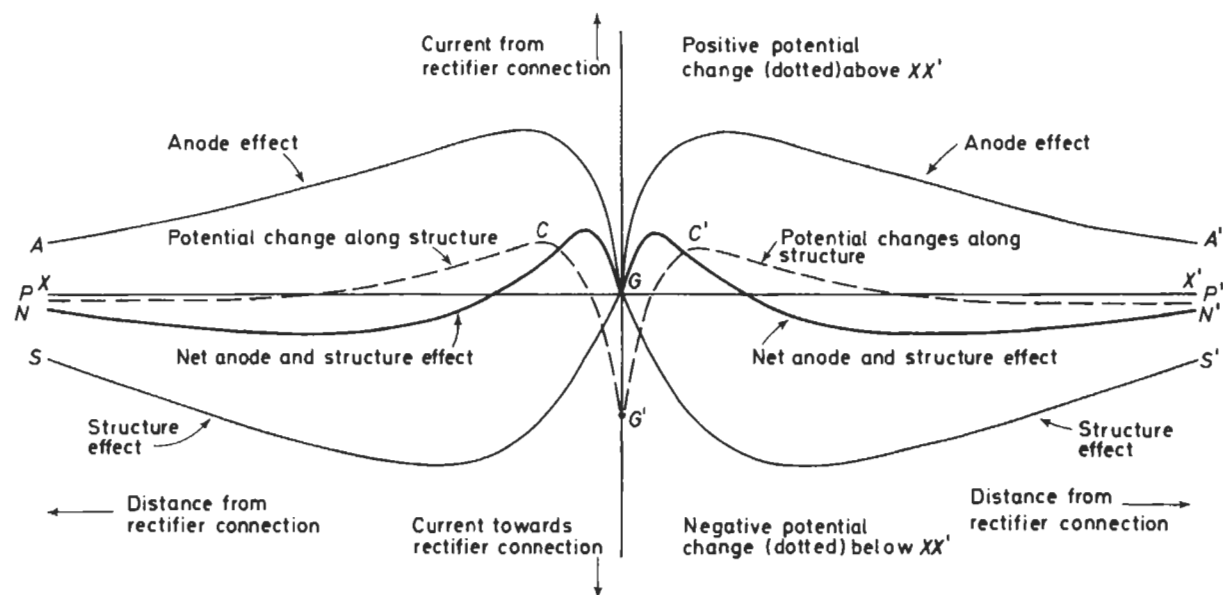


Fig. 10.39 Change of current and potential of an unconnected structure near a groundbed due to cathodic-protection interaction. Note that the dashed curve $PCG'C'P'$ gives the potential changes along the structure and that the maxima at C and C' are the maximum positive changes in the structure/soil potentials and that they correspond with the points of maximum gradient on the net current curve NGN' . Note also that 'Current from rectifier connection' does not mean that structure is connected to the rectifier

point opposite the connection to the protection equipment. If the two structures are not parallel, positive or negative changes of potential will also occur at crossings and at other places where the structures are electrically close to each other.

The amount of interaction caused by a protection scheme using galvanic anodes will be much less than that involved in the case of impressed-current protection, because of the low current output obtained from each anode. Significant positive potential changes have, however, been measured on nearby structures in cases where galvanic anodes are closely spaced and the distance between structures is small.

The severity of corrosion interaction will depend on the density of the stray current discharged at any point on the secondary structure. This may be assessed by measuring the changes in structure/soil potential due to the application of the protection current. Potential tests should be concentrated on the portions of pipe or cable which are close to the structure to be cathodically protected, where the potential change is likely to be more positive.

Since the interaction tests may require the co-operation of owners of protected and unprotected structures, it is advisable to agree on the testing apparatus and methods to be employed. This is facilitated in the UK by a Joint Committee composed of representatives of the major underground services. The Committee receives active assistance from the D.T.I. and from a number of national research associations. Criteria have been agreed for determining the acceptability or otherwise of potential changes on installations buried near cathodically-protected structures. Recommendations³ have been published by the Committee on testing methods and equipment, on the information that should be supplied to the interested authorities when a cathodic-protection scheme is being installed, and on methods of avoiding interaction.

The relationship of anode current density with electrode potential for mild steel in dilute aqueous soil electrolytes has been studied by Hoar and Farrer⁴. The study shows that in conditions simulating the corrosion of mild steel buried in soil the logarithm of the anode current density is related approximately rectilinearly to anode potential, and the increase of potential for a ten-fold increase of current density in the range 10^{-5} to 10^{-4} A/cm² is between 40 and 65 mV in most conditions. Thus a positive potential change of 20 mV produces a two- to three-fold increase in corrosion rate in the various electrolyte and soil solutions used for the experiments.

The results of these experiments have been considered by the Joint Committee for the Co-ordination of the Cathodic Protection of Buried Structures and, in view of the various types of buried structures concerned and the circumstances in which field tests are conducted, the Committee decided not to amend its provisional recommendation that when cathodic protection is applied to a buried structure the maximum permissible potential change in the positive direction on a nearby pipe or cable should be 20 mV. If there is a history of corrosion on the unprotected installation no detectable positive change in structure/soil potential should be permitted. These criteria of interaction have been adopted in the British Standard Code of Practice for Cathodic Protection⁵.

The adoption of a maximum permissible positive potential change of 20 mV is based on theoretical and laboratory studies. However, there is evidence to show that in practice changes of + 20 mV do not appear to cause

noticeable corrosion damage even after the passage of many years, and in some countries larger changes with values of up to +100 mV, are accepted. The rate of corrosion depends on the density of the current exchanged between structure and electrolyte and no practicable method has yet been found for measuring this. However, some account should be taken of the resistivity of the electrolyte and studies are being made to devise a better criterion based on potential change and also on the resistivity of pipe coatings, cable wrappings and soil.

Methods of Preventing or Reducing Interaction⁶

Interaction tests should be made on all unprotected structures in the vicinity of a proposed cathodic protection installation, and should be repeated annually or at some other suitable interval to ensure that alterations in the layout of plant or in the electrical conditions are taken into account. It is most convenient if the tests on all unprotected pipes or cables are made at the same time, the potential measurements being synchronised with the regular switching on and off of the protection current. It may then be convenient to continue with further tests to confirm that any remedial measures applied to one installation do not adversely affect other installations.

A number of methods may be used to reduce the interaction on neighbouring structures. In some circumstances it may be practicable to reduce the current output applied to the protected structure or to resite the groundbed so that the anode effect on an unprotected pipe or cable is altered as required*. The physical separation between the groundbed and nearby buried structures can be increased by installing anodes at the bottom of deep-driven shafts and substantial improvements can be made using this technique.

The electrical resistance between the structures at crossing points or elsewhere can be increased by applying insulating wrappings. If the wrappings are applied only to sections of the unprotected structure where a positive change in potential is measured, the wrapping must ensure uniformly high insulation in order to avoid localising the anodic attack at pinholes or similar discontinuities.

If the positive potential changes are very small and confined to a few points on a small unprotected structure, it may be practicable to reduce the potential at these points by installing reactive anodes. The anodes will probably be most effective if they can be buried between the two structures. In some circumstances a similar screen of zinc, aluminium or steel may be installed between the structures. The screen must be electrically connected to the unprotected structure since it is installed with the object of providing an electrolytic path to earth for the interaction current.

If both buried structures have been subject to corrosion damage the best solution may be to install a joint cathodic-protection scheme with sufficient current output to provide adequate protection for both installations. The application of separate cathodic-protection schemes to structures buried

* Although the geometry of buried structures cannot be altered the groundbed can be placed so that the anode effect and the structure effect on the unprotected structure tend to balance each other.

close to each other is liable to cause interaction damage because of variations in current output on the two systems. This may be avoided by connecting the two structures together at several points.

In the UK the most common method of reducing interaction is to connect the protected and unprotected structures together by means of metallic bonds. This method is more successful if care has been taken to ensure that the unprotected structure is electrically continuous. If possible, bonds should be connected to points on the unprotected structure where maximum positive changes in potential are observed, but it may be more practicable to install a shorter bond between points where access can conveniently be obtained for periodic inspection and tests.

If one of the structures to be bonded is the sheath or metallic armouring of an electric supply cable, special precautions will be necessary to ensure that the voltage rise at the bond in the event of an instantaneous earth fault on the power-supply system does not endanger personnel or equipment associated with other buried structures. The bond and any associated current-limiting device should be suitably insulated and of adequate current-carrying capacity.

Account must also be taken of small alternating currents which may be diverted from the sheath of a power supply cable by a bond connected to nearby buried structures. Such currents may be sustained for long periods and if they are diverted to the sheaths of telecommunication cables noise may be induced in the telephone circuits.

If the electrical continuity of a buried pipe or cable is broken at a point where a.c. is liable to flow owing to the presence of a bond, the gap should be bridged by means of a continuity bond. This will prevent the appearance of a dangerous voltage between the two sections of pipe or cable.

Interaction due to the use of reactive anodes can best be avoided by careful siting of each anode during installation. In particular, anodes should not be buried close to a point where the protected structure crosses an unprotected structure, nor should anodes be so placed that an unprotected pipe or cable passes between the anode and the protected installation.

Conclusions

Recent experience has confirmed that, by adopting the recommendations of the British Standards Institution⁵ or similar codes of practice operating in other countries, the likelihood of corrosion damage to buried structures adjacent to cathodically protected installations is negligible. This is because recently installed cathodically protected structures are usually coated with efficient and durable insulating coverings such as epoxy resins and the protective current applied is consequently small. In many cases the small protective currents that can be applied by means of galvanic anodes is adequate.

Nevertheless, special consideration should be given to any measured small positive changes in structure/soil potential on a nearby buried pipe or cable if there is reason to believe that the secondary structure is already corroding because of local soil conditions, or as a result of stray currents from another source.

In many cases the results of interaction tests may not appear to conform with the theoretical considerations described earlier in this chapter. This is because of non-uniform spacing and depth of the buried structures and the presence of crossing points. The position of the groundbed and local variations in soil resistivity and insulating coatings will also modify the test results.

J. R. WALTERS

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2. Pope, R., *Corrosion*, 6, 201 (1950)
3. Joint Committee for the Co-ordination of the Cathodic Protection of Buried Structures, London, Recommendations Nos. 1, 2, 3 and 4
4. Hoar, T. P. and Farrer, T. W., *Corros. Sci.*, 1, 49 (1961)
5. *Code of Practice for Cathodic Protection*, CP 1021, B.S.I., Aug. (1973)
6. C.C.I.T.T. *Recommendations Concerning the Construction, Installation and Protection of Telecommunication Cables in Public Networks*, I.T.U., Geneva (1974)

10.7 Cathodic-protection Instruments

A number of measurements, principally electrical, are necessary in order to ensure that a cathodic-protection system is correctly designed and will provide full protection to the structure concerned, and to determine accurately the effect of such a system on other structures. This section deals with the instruments used for making these measurements and indicates in general terms the various types available to the corrosion engineer today. Brief details of instruments not directly connected with cathodic protection as such, but nevertheless associated with it, are also included.

Basic Requirements

All instruments used in cathodic-protection work must be accurate, reliable and easy to maintain.

For cathodic-protection work the best instruments are calibrated to an accuracy of 0.5% or less of full-scale deflection. In addition, scales are usually so selected that the majority of the readings taken fall within the upper half of the scale, where the least error will occur. Second-grade instruments are usually calibrated to an accuracy of approximately 2% of full-scale deflection.

Most instruments used in cathodic-protection work are essentially field instruments, and must therefore be portable and sufficiently robustly constructed to withstand rough handling and to be capable of operating reliably under a wide range of climatic conditions.

As far as possible instruments should be so constructed that repairs or replacements can be made quickly, and standard, readily obtainable components should be used.

Theory of d.c. Indicating Instruments

The application of cathodic protection generally involves the use of direct current. The movement in nearly all instruments used in cathodic protection is therefore of the moving-coil permanent-magnet type, which gives coil deflection (and thus pointer deflection) proportional to the current in the coil.

Damping of the movement to prevent overswing or oscillation of the needle is provided by the eddy currents induced in the metal former on which the coil is wound, and further damping (i.e. critical damping) can be obtained by placing a low resistance across the coil. The main advantages of this type of instrument are uniformity of scale, high torque: weight ratio, and low power consumption.

By the insertion of suitable shunts and/or resistances it is possible to use one instrument to measure both current and voltage over a wide range.

The coil (wound on a light metal former) can be suspended by a fine strip of phosphor bronze between the pole pieces. Attached to this suspension is a small mirror which reflects on to a scale a beam of light which is focused upon it. An instrument of this kind is known as a D'Arsonval galvanometer and is used in potentiometer circuits and various methods of measurement of resistance.

The use of a light beam as an indicator avoids the errors caused by friction with a normal pointer, while a hairline incorporated in the projection lens eliminates errors due to parallax, and with the scale at a distance of 1 m from the mirror, a sensitivity of up to 1 500 mm/ μ A can be achieved.

This instrument, as described above, is quite unsuitable for field measurements.

Types of Instruments

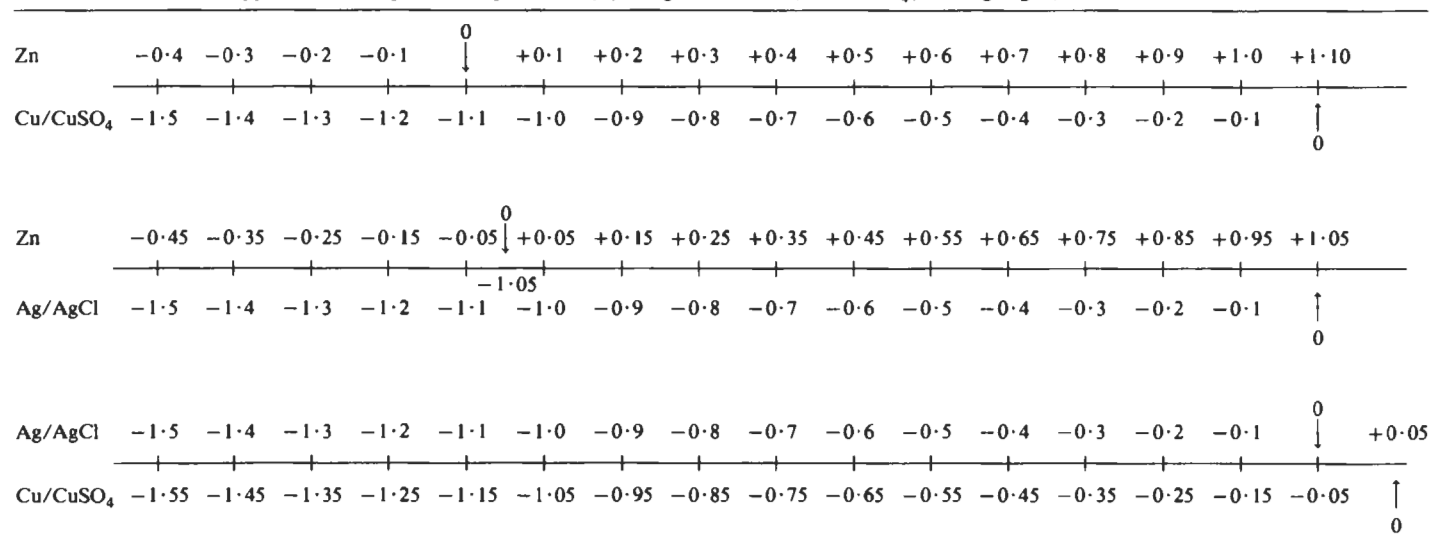
Cathodic-protection instruments may be classified as potential-measuring, current-measuring, resistance/conductance-measuring, multicomination, recording and ancillary.

The various types are dealt with in some detail in the following pages. Except where noted, the instruments have a moving-coil movement.

Potential-measurement Devices

Reference electrodes The generally accepted criterion for the effectiveness of a cathodic-protection system is the structure/electrolyte potential (Section 10.1). In order to determine this potential it is necessary to make a contact on the structure itself and a contact with the electrolyte (soil or water). The problem of connection to the structure normally presents no difficulties, but contact with the electrolyte must be made with a reference electrode. (If for example an ordinary steel probe were used as a reference electrode, then inaccuracies would result for two main reasons: first, electrochemical action between the probe and the soil, and second, polarisation of the probe owing to current flow through the measuring circuit.)

Figure 10.40 shows two patterns of the Cu/CuSO₄ half-cell and Fig. 10.41 an Ag/AgCl, Cl⁻ half-cell; both are commonly used as reference electrodes. The illustrations are intended only to show the general features of the many different patterns commercially available. Table 10.29 gives a comparison of the potential of a structure measured against Cu/CuSO₄(sat.), Ag/AgCl, KCl(sat.) and corroding pure Zn, which is widely used as a reference electrode in chloride environments.

Table 10.29 Approximate comparison of potentials (V) using Zn/seawater, Cu/CuSO₄, and Ag/AgCl, sat. KCl reference electrodes*

* If the potential of the structure is found to be +0.4 V vs. Zn it will be -0.7 V vs. Cu/CuSO₄, sat., and -0.65 V vs. Ag/AgCl, sat., KCl. Approximate values of the above reference electrodes on the Standard Hydrogen Scale (S.H.E.) are as follows: Cu/CuSO₄, sat. = 0.30-0.32 V; Ag $\frac{1}{2}$ AgCl, sat. KCl = 0.020 V (0.025 V in sea-water); Zn/sea-water = -0.75 V.

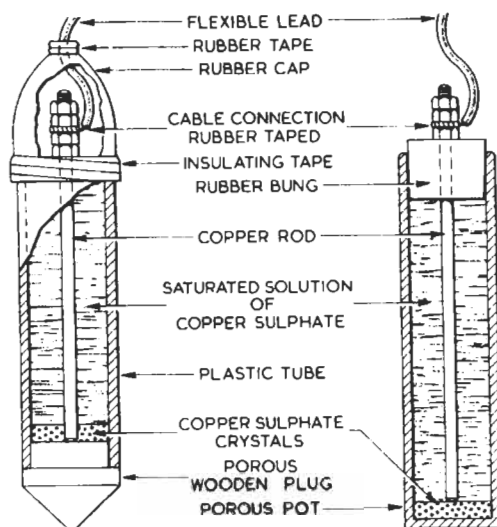


Fig. 10.40 Copper/copper sulphate half-cells

From Fig. 10.40 it will be seen that contact between the electrolyte (soil or water) and the copper-rod electrode is by porous plug. The crystals of CuSO_4 maintain the copper ion activity at a constant value should the half-cell become polarised during measurements. The temperature coefficient of such a cell is extremely low, being of the order of $1 \times 10^{-5} \text{ V/}^\circ\text{C}$ and can thus be ignored for all practical purposes. To avoid errors due to polarisation effects, it is necessary to restrict the current density on the copper rod to a

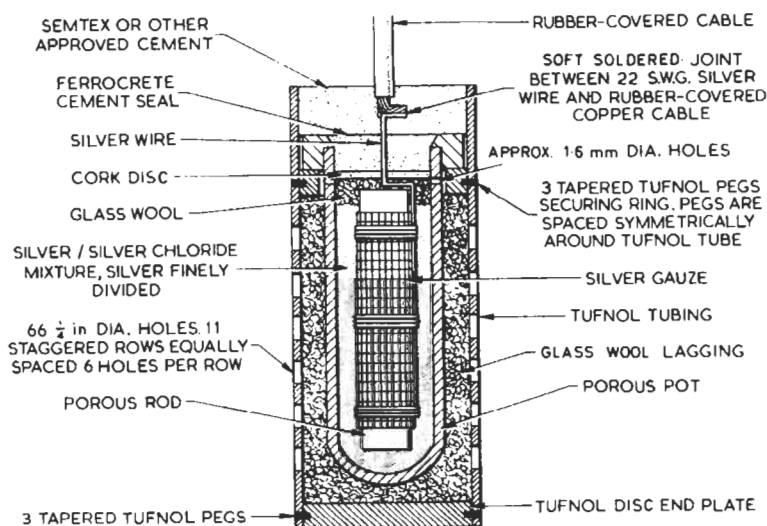


Fig. 10.41 Silver/silver chloride half-cell (Admiralty pattern). The electrode is immersed in a chloride-containing solution which diffuses through the porous pot and thus comes into contact with the Ag/AgCl mixture

value not exceeding $20 \mu\text{A}/\text{cm}^2$. The Cu/CuSO_4 half-cell is in almost universal use for measurement of structure/electrolyte potentials on buried structures. Its main advantages are that it is cheap and simple to construct, that the materials are easily obtainable, and that it can be quickly made up at any time.

The $\text{Ag}/\text{AgCl}, \text{Cl}^-$ half-cell has a chloridised silver electrode which is generally immersed in either a saturated potassium chloride solution or a mixture of finely divided silver and silver chloride. This type of half-cell is normally used for measurement of structure/electrolyte potentials of immersed structures, contact between the half-cell and electrolyte (fresh or sea-water) being made through the walls of a porous pot enclosing the cell. For measurements in sea-water a chloridised silver electrode is used and the electrode is immersed directly in the water thus dispensing with the saturated KCl solution; the electrode is prepared by fusing silver chloride onto a silver mesh and partially reducing the silver chloride by cathodic polarisation.

The $\text{Ag}/\text{AgCl}, \text{Cl}^-$ electrode is probably the best reference electrode for measuring potentials of waters at elevated temperatures.

One further type of reference electrode is the zinc half-cell which consists merely of a high-purity zinc rod. Such an electrode will maintain a constant potential after a short 'settling down' period following installation (particularly in sea-water). The main advantages of a zinc reference electrode are that it requires no special preparation and no subsequent remaking during its life. It is ideal for use as a permanent reference electrode installed on a cathodic-protection scheme, as for example the water box of a large heat exchanger, where inspection is infrequent and access to the structure while it is operating is impossible. It should be noted that in the case of zinc the potential is a *corrosion* potential, whereas in the case of the other reference electrode the potential is a *reversible* potential (see Section 20.3). In practice, it is therefore an advantage to maintain the surface of the zinc in a slightly active condition by deliberately reducing the impedance of the measuring circuit. Generally the zinc electrode is used where the electrolyte surrounding the protected structure is water, as this ensures good contact with the electrode. Its use in soils is generally restricted to damp ground and it cannot be recommended as reliable in dry soils, even when placed in a special backfill.

Voltmeters and potentiometers The instruments described here are generally referred to as *corrosion voltmeters*. As mentioned previously, the current flowing through any potential-measurement circuit must be small to avoid errors due to polarisation. Moreover, if the current flow is too large, errors will be introduced owing to the voltage drop caused by the contact resistance between the reference electrode and the electrolyte. It is thus clear that the prime requirement of a potential measurement circuit is high resistance.

For a direct-reading instrument, sensitivity should be at least of the order of $50 \text{ k}\Omega/\text{V}$, and instruments are commercially available with sensitivities of up to and exceeding $1 \text{ M}\Omega/\text{V}$. Direct-reading meters are usually made to show several ranges, which are obtained by the use of suitable resistances placed in series with the indicating instrument (Fig. 10.42).

To measure structure/electrolyte potentials with electrolyte resistivities in excess of $2 \text{ k}\Omega \text{ cm}$, a high-resistance potentiometer unit as shown in Fig. 10.43 or a potentiometric voltmeter as illustrated in Fig. 10.44 may be used.

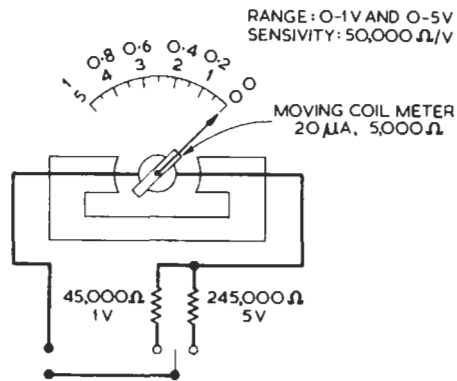


Fig. 10.42 Direct-reading voltmeter

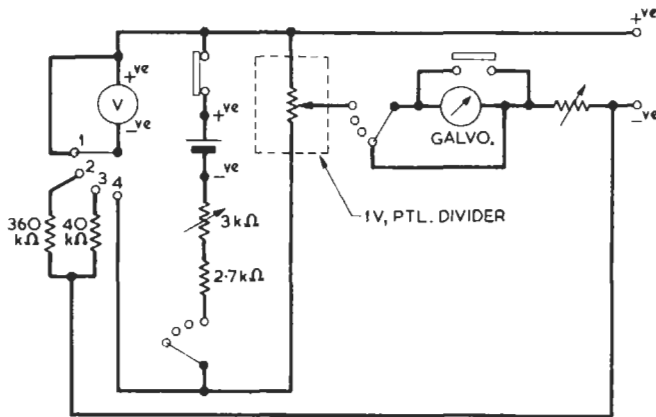


Fig. 10.43 Potentiometer voltmeter (courtesy of The Post Office)

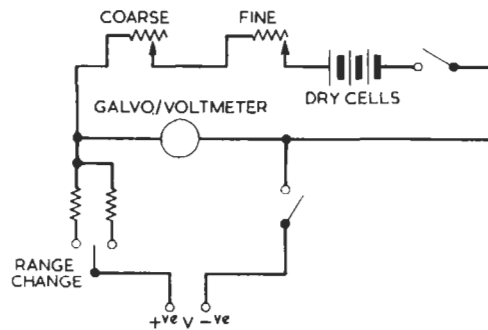


Fig. 10.44 Basic circuit potentiometer voltmeter

In both types of instrument the voltage to be measured is balanced against an external applied voltage (usually from batteries within the instrument). At balance, no current flows through the external circuit and thus errors due to contact resistance are eliminated.

The potentiometer must be calibrated against a standard cell, while with the potentiometric voltmeter the voltage to be measured is balanced against a battery e.m.f., using uncalibrated resistors and the voltmeter as a galvanometer. At balance the voltage is transferred to the voltmeter and read direct. The magnitude of voltage which can be measured by both instruments is limited by the maximum voltage of the (usually) dry cell which they contain. It is, however, possible to extend the range by using a potential divider or *volt box*.

For normal field work the potentiometric voltmeter is the more popular instrument, being usually of lighter construction and not requiring calibration against a standard cell. Where extremely small potentials (usually potential shifts) of the order of 1 mV are to be measured, however, the potentiometer is more suitable and accurate.

Valve voltmeters were widely used in the past, but have been replaced by transistor voltmeters. With instruments of this type it is possible to achieve an input resistance of 50 M Ω or more, the current required to operate the instrument being of the order of 10^{-14} A. The early instruments had a tendency to zero drift on the lower ranges, but this has been overcome in the modern transistor types. Such instruments are most often used to make potential readings in extremely high-resistance electrolytes. The accuracy of such instruments is of the order of 2% full-scale deflection. It is necessary to ensure that both types are so designed that they do not respond to alternating currents.

The technique adopted in measuring structure/electrolyte potential is illustrated in Fig. 10.45. While it is not truly within the scope of this chapter,

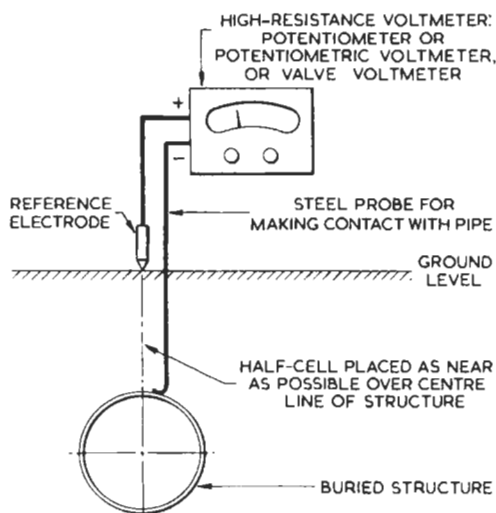


Fig. 10.45 Measurement of structure/electrolyte potential

it is as well to note that the position of the reference electrode in relation to the structure is important. Theoretically the half-cell should be placed as near to the structure as possible (i.e. within a few millimetres) to avoid IR drop in the electrolyte. This is often not possible in practice as, for example, with a buried pipeline. In such a case, the cell should be placed in the soil directly over the structure, and it is wise to allow a 'safety factor' of say 50 mV over and above the minimum protective potential to compensate for IR drop.

Current-measuring Instruments

These may be classified generally according to whether they are used to measure current delivered or drained by a structure under protection, or to measure current flowing within the structure itself.

By the use of suitable shunts, the basic moving-coil movement can be adapted to measure an almost unlimited range of currents. Figure 10.46 illustrates a direct-indicating instrument with shunt, to measure current up to 5 A d.c. To ensure that the resistance of the circuit is not materially altered by the insertion of an ammeter, it is usual to install either a shunt or the meter itself (usually a moving-coil meter with internal shunt) permanently in the circuit. Ammeter shunts are normally of the four-terminal type, to avoid contact resistance errors, i.e. two current terminals and two potential terminals, as shown in Fig. 10.46.

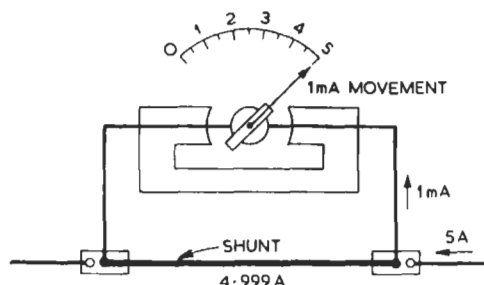


Fig. 10.46 Direct-indicating instrument

In making measurements of current flowing within a structure, it is extremely important that additional resistance, as for example a shunt, is not introduced into the circuit, as otherwise erroneous results will be obtained. One method is to use a tong test meter. Such instruments are, however, not particularly accurate, especially at low currents, and are obviously impracticable in the case of, say, a 750 mm diameter pipeline. A far more accurate method and one that can be applied to all structures, is the zero-resistance ammeter or, as it is sometimes called, the *zero-current ammeter* method. The basic circuit of such an instrument is shown in Fig. 10.47.

From Fig. 10.47 it will be seen that if I_b is adjusted until there is zero voltage on the voltmeter, then $I_s = I_b$. When this type of instrument is used

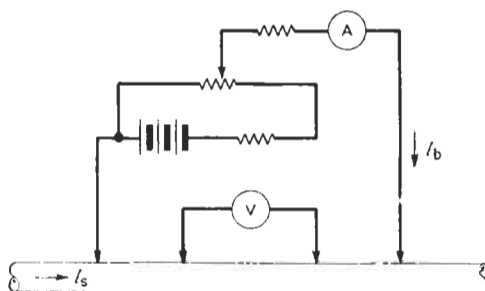


Fig. 10.47 Zero-resistance ammeter

to measure current in, say, a bond between one structure and another, if simultaneous measurements are made at locations on the structure (i.e. interference testing) inaccurate results will be obtained. This is because at balance there is no current in the structure at the measurement point, and this could materially alter the current distribution to the structure.

Where measurements of current in massive structures having extremely low longitudinal resistances are required, and to avoid the errors referred to in the previous paragraph, a refinement of the zero-resistance ammeter is used. Instead of a voltmeter, a high-sensitivity D'Arsonval galvanometer with a centre-zero scale is used. The connections remain essentially the same as those in Fig. 10.47, except that a reversing switch is incorporated so that the current I_b can be applied first in one direction and then in the other.

Let I_s = current in structure, let I_b = meter current (calibrating current), let deflection of the galvanometer due to I_s be A_0 (note that the direction of deflection will indicate the direction of current flow), and let the deflection of the galvanometer with I_b applied in both directions be A_1 and A_2 , then:

$$A_1 = I_b + I_s \text{ (say)}$$

and thus

$$A_2 = I_b - I_s$$

therefore

$$A_1 + A_2 = 2I_b$$

Thus calibration of galvanometer in amps or milliamps per division deflection is

$$2I_b / (A_1 + A_2)$$

therefore

$$I_s = A_0 [2I_b / (A_1 + A_2)]$$

The zero-resistance ammeter is seldom employed for routine testing. This instrument requires careful handling to avoid damage, in particular to the galvanometer. Usually two permanent test leads are installed at a set distance apart, and by the initial use of a zero-resistance ammeter a calibration chart of potential between the two leads and current in the structure is drawn up. Thus when routine testing is made, it is only necessary to measure the

potential difference between the leads. The current so measured will not be truly accurate, owing to the minute current in the measurement circuit, but for all practical purposes this can be ignored.

Resistivity/Conductivity-measuring Instruments

Instruments in this category are used for the measurement of electrolyte resistivity, resistance, and insulation (i.e. protective-wrap) conductivity.

Measurement of resistivity The most usual method of measuring soil resistivity is by the four-electrode 'Wenner' method. Figure 10.48 indicates the basic circuit. The mean resistivity R_M is given by

$$R_M = 2a(E/I)$$

where I is the current applied between the current electrodes C_1 and C_2 , and E is the potential developed between the potential electrodes P_1 and P_2 by the current I^* . The value given by this method is the average resistivity of the soil to a depth a equal to the spacing of the electrodes. It is most important to note that for accurate and consistent results, the electrodes must be equidistant from one another and placed in a straight line. This relatively simple set-up, illustrated in Fig. 10.48, suffers from inaccuracies arising from polarisation of the potential electrodes and effects of possible stray currents in the soil. To minimise these, the electrodes used for measuring potential P_1, P_2 should be Cu/CuSO₄ half-cells, and reverse polarity readings should be taken. One source of inaccuracy that cannot be overcome with this method is that due to the contact resistance of the potential electrodes P_1 and P_2 to earth.

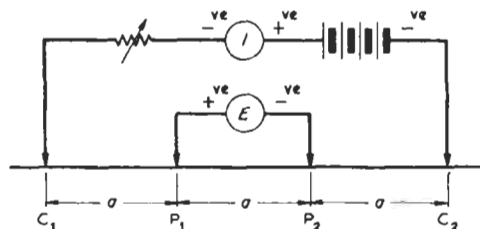


Fig. 10.48 'Wenner' method. Normally C_1, C_2 and P_1, P_2 are steel rods, but for higher accuracy Cu/CuSO₄ electrodes should be used for P_1, P_2

To avoid the errors of polarisation and stray currents, special resistivity meters are employed. One form of these uses an alternating current produced from batteries by a vibrator. The effective resistance is measured by a modified Wheatstone bridge with balance indicated by a galvanometer.

A further type of instrument employs a hand-generated current passed through the current coil of an ohmmeter and then through a current reverser so that an alternating current is delivered to the current electrodes. The alternating current due to alternating potential between the potential electrodes

* For proof of this equation, see Wenner, F., *Nat. Bur. Stand. Publn.*, 12, US Dept. of Commerce, 496 (1915).

is then rectified by a commutator mounted on the generator shaft, and the current is passed through the potential coil of the ohmmeter. Thus the deflection of the instrument is the ratio of IR/I , or resistance R . To compensate for resistance to earth of the potential electrodes, the ohmmeter is connected directly across these potential electrodes. The resistance is adjusted (by means of a variable resistance) to a set value, which is usually denoted by a mark on the meter scale so that the resistance in the potential circuit is at the predetermined value used in calibrating the instrument. A circuit diagram is given in Fig. 10.49, but it should be noted that this type of device is now being replaced by solid-state battery-powered versions.

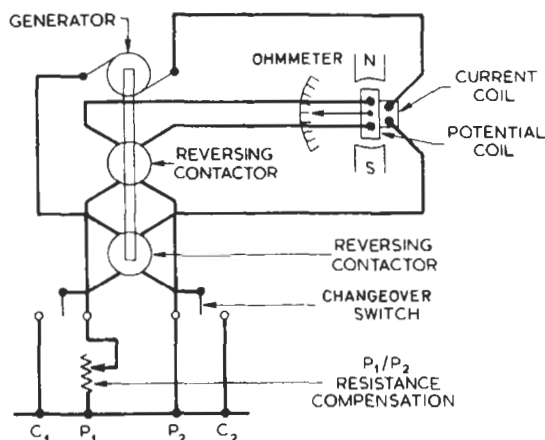


Fig. 10.49 'Megger' earth resistivity meter (courtesy Evershed and Vignoles)

Soil resistivity may be measured by an instrument known as the *Shepard Cane* resistivity meter, which uses only two electrodes. In principle, the instrument operates by measuring, with a low-resistance ammeter, the current flowing between two electrodes placed a set distance (usually 0.3 m) in the soil. To avoid polarisation effects the positive electrode has a very small area and the negative electrode a large area. This instrument is of light construction, and is easily portable and simple in use. Normally, however, it will indicate resistivity only near the surface, and it is of use only in giving a general indication. The basic circuit diagram of a Shepard Cane is given in Fig. 10.50.

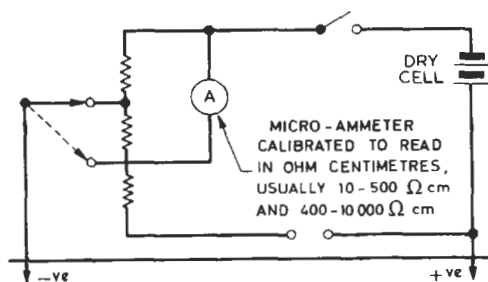


Fig. 10.50 Shepard Cane resistivity meter

To avoid errors due to polarisation, the instrument can be used with a vibrator to provide an alternating potential between the electrodes, in which case the areas of the electrodes can be the same.

A variation of the Shepard Cane incorporates both electrodes on a single rod. A circuit diagram of this type of instrument is shown in Fig. 10.51. The single rod has a calibration constant, determined by the area of the positive electrode. At balance the resistivity is given by the resistance multiplied by the rod constant. This instrument is portable and simple to operate, but it cannot be recommended when accurate results are required.

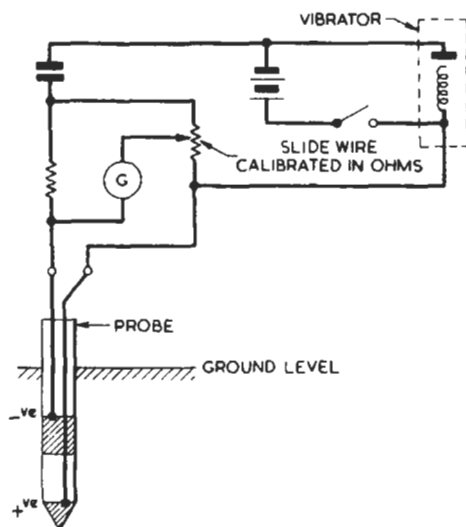


Fig. 10.51 Single-rod resistivity meter

Resistivity of an electrolyte can also be measured by passing a known current through a known length and cross-section of the electrolyte, and measuring accurately the voltage drop across the length. It is preferable to use alternating current to avoid polarisation effects. Alternatively, the resistance of a known length and cross-section of the electrolyte may be measured directly by using a four-electrode instrument with the potential and current electrodes P_1 , C_1 and P_2 , C_2 joined together in such a way that the instrument will measure resistance as a normal ohmmeter. Special cells also exist for use with resistivity meters, which are so constructed and calibrated that resistivity can either be read directly from the instrument or simply calculated from the product of the measured resistance and known cell constant. Measurements of resistivity on samples, as just described, will give accurate results only on liquid electrolytes and cannot be recommended for use on soil samples, where the value of resistivity measured will vary with the degree of compaction of the soil.

Measurement of resistance As previously mentioned, the four-electrode resistivity meters can be used to measure resistances. For this purpose the

most accurate instrument is the hand-generator type, as it usually has a large clear scale calibrated directly in ohms. Most vibrator-type instruments, however, rely on a calibrated dial and galvanometer and on low ranges the exact point of balance is often difficult to determine with any accuracy.

The accurate measurement of resistance can of course be carried out by means of a Wheatstone bridge, Carey Foster bridge, or a similar arrangement.

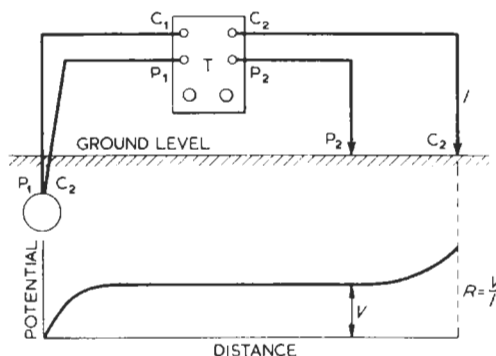


Fig. 10.52 Measurement of resistance of structure to remote earth

The measurement of resistance to remote earth of a metallic structure is normally carried out with a four-electrode instrument. The connections are shown in Fig. 10.52. A current I is passed between the structure and a remote electrode. The potential difference V is measured between the structure and a second remote electrode. In this way the ohmmeter records the resistance of the structure to earth, i.e. V/I . The spacing of the electrode from the structure is important and must be such that the remote potential electrode lies on the horizontal part of the resistance/distance curve, as shown in Fig. 10.52. Generally speaking, a minimum distance of 15 m from the structure is necessary for the potential electrode to lie on the flat part of the curve, with the current electrode usually at least twice the distance of the potential electrode.

Measurement of conductivity The measurement of electrolyte conductivity — the reciprocal of the resistivity — is a fairly simple matter, being calculated from the resistivity as measured by some of the methods described above.

Often it is necessary in designing a cathodic-protection system to know the conductivity of a protective coating (e.g. bitumen enamel) on a structure. This measurement is usually carried out by finding the resistance between an electrode of known area placed in contact with the coating and the structure itself. The electrode placed on the structure can be either of thin metal foil or, preferably, of material such as flannel soaked in weak acidic solution. The resistance between the pad and the metal is measured by means of either a resistivity meter, as previously described, or a battery with a voltmeter and an ammeter or microammeter. Generally speaking, in field work where such measurements have to be made, a resistivity meter is preferable.

Multicombination Instruments

As their name suggests, these instruments are capable of carrying out a variety of measurements, e.g. structure/electrolyte potentials, current, resistivity and voltage. Most instruments of this type contain two meters in one case, one being a low-resistance millivolt/voltmeter and milliamp/ammeter, and the second a high-resistance voltmeter.

The advantages of this type of instrument are (a) that only one instrument is required for all necessary measurements, and (b) that it is portable and thus particularly suitable for field work.

The main disadvantage is that should a fault occur in one circuit of the instrument the complete instrument is often rendered inoperative.

Recording Instruments

Miniaturisation of electronic components has enabled the construction of a compact, portable, battery-operated recording voltmeter. The principal use of this instrument is to measure pipe/soil potential fluctuations over a period of time. The instrument can be modified to measure current variations.

Ancillary Instruments

Apart from the instruments described in previous paragraphs, there are others that, while not directly connected with cathodic protection as such, are extremely useful tools to a corrosion engineer. They include pH meters, Redox probes, protective-coating test instruments and buried-metal-location instruments.

High-voltage coating-testing equipment When cathodic protection is applied to a structure which has a protective coating, the current required is proportional to the bare metal area on the structure. Thus whenever a protective coating is applied it should be of good quality, with very few failures or pin holes in it, so that the cathodic-protection system may be economic.

It is now fairly standard practice, particularly in the case of pipelines, to carry out an inspection of the protective coating (after application) with a high-voltage tester, known as a *holiday detector*. Basically, a high voltage is applied between an electrode placed on the coating and the structure. At any 'holidays' (flaws) in the coating, a 'spark over' occurs and is usually accompanied by a visual or audible alarm. For pipelines, the electrode often takes the form of a rolling spring clipped round the pipe. Other electrodes are in the form of wire brushes.

The high voltage is obtained either by a step-up transformer from the mains, or a motor-generator set, or alternatively from batteries and a vibrator with a high-tension coil. The battery-operated instruments, are most popular as they are easily portable and most suited for field use. Such an instrument is illustrated in Fig. 10.53.

For the examination of paint films or special coatings, e.g. pipe linings, low-voltage holiday detectors with wet sponge electrodes are available.

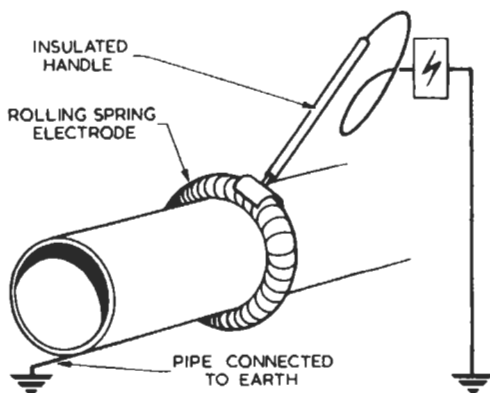


Fig. 10.53 Holiday detector

The choice of voltage for use with a holiday detector depends on the thickness and type of coating applied to the structure. As a guide, in the case of pipelines, a voltage equivalent to approximately 5 kV/mm thickness is used in testing a coal-tar coating.

Buried metal locating instruments Instruments in this category are used to locate buried metallic structures, to detect possible electrical discontinuities in buried structures, to locate possible junctions or points of contact between one structure and another, and to indicate the condition of a protective coating applied to a buried structure. A signal of a given frequency to a buried structure is either injected or induced into the structure and traced with a search coil and earphones. Most instruments use a high-frequency signal of 1 kHz or higher, although one or two use a simple interruptor. The transistor has made it possible to make very compact portable battery-operated instruments.

Recent Developments

Cathodic protection and associated instruments have developed in-line with the changing monitoring demands of both the onshore and offshore industries. In particular, for potential and current density measurements, far greater quantities of data are sought and are required to be processed into an easily assimilated form. Thus cathodic protection instrumentation has benefited from an increased association with microprocessor-based data handling and storage systems.

Reference Electrodes

The principle reference electrodes used in the onshore and offshore industries have remained unchanged. The Cu/CuSO₄ cell is used almost exclusively onshore in the form based on the plastic tube and porous wooden plug illustrated in Fig. 10.40, although certain potential survey instruments have

required the development of this form into 'ski-stick' electrodes. In addition, Cu/CuSO₄ cells are produced with ceramic porous plugs for increased life and increased diameter, in order to reduce contact resistance with high resistivity soils.

Permanently installed electrodes are increasingly used, and construction of these items can be based on long lengths, approximately 30 m, of spirally coiled copper wire set in a gel of saturated copper sulphate, contained in a porous terracotta pot.

Offshore, both Ag/AgCl and metallic zinc electrodes are used for potential measurements and are also employed for current density surveys undertaken on the offshore platforms and pipelines, as discussed below. It has been found beneficial for offshore applications to install together an electrode of each type on a structure, one acting as a function check on the other¹.

The electrodes designed for permanent installation on deep-water structures must be protected from damage but must also correctly 'view' the protected structure. Thus electrodes must be closely placed to the structure to avoid the incorporation of an '*IR*' element in the potential measured, but must not create a 'protection' shadow which could cause a false indication of the protection level.

Commercially available electrodes are produced in coated fabricated steel housings in which the electrodes are retained by hard-setting epoxy resins. Connecting cables pass from the housing through cable glands and are either installed in conduits to the surface or are wire armoured for protection.

Potential Measurement Devices

For field measurements, the popular analogue potentiometric voltmeter has been largely superseded by the electronic digital-display multimeter. Many commercially available multimeters, not specifically designed for cathodic protection measurements, are generally suitable. The d.c. voltage ranges normally included are 200 mV, 2 V and 20 V, displayed on a 3½ digit liquid-crystal display. Typical resolution is 100 µV on a 200 mV range, with an accuracy of 0.25% of the reading plus one digit. All these ranges will typically have input impedances of at least 22 MΩ, ensuring minimal errors in all but the highest resistivity electrolytes. For high-resistivity electrolytes some electronic multimeters are provided with a selectable range of input resistances, so that any errors in readings due to high resistance in the external circuit may be detected.

Meters must be provided with adequate a.c. rejection on d.c. ranges. This is typically, greater than 60 dB for 50/60 Hz in the normal mode and greater than 100 dB for common inode rejection.

Hand-held multimeters are available with robust, waterproof cases, well-suited for field use.

One of the more recent developments in potential measurement instruments has been their incorporation into what is best described as 'data management devices'. These units will not only display a potential reading but may be instructed to store this information for later retrieval and processing. The complete unit incorporates a high-impedance voltmeter with an integral microprocessor for data and code entries into a solid-state

memory. Data and codes are inputted by the use of an alpha-numeric keyboard, although auxiliary data may also be inputted via a light-pen bar-code reader. Bar codes are used, for example, at test points to store identification data. More sophisticated units are provided with real-time clocks and can automatically store electronically entered data and time, under time clock control.

Potential data loggers are now available to undertake close interval pipeline surveys. These increasingly popular surveys, determine a pipeline's pipe-to-soil potential at nominal intervals, of as little as 1 m. Additional information is gained by the recording at each point, of both the pipe-to-soil potential with the cathodic protection system 'ON', together with the potential some 100–300 ms after the cathodic protection system is switched 'OFF'. This 'instantaneous' 'OFF' potential being devoid of any *IR* drop component present in the 'ON' potential measurement.

Typical mobile data loggers are based on the integration of a high impedance voltmeter with an electronic solid state battery-backed memory sufficient for the collection of over 10 000 measurements. Measurements are taken with reference to one of two parallel connected 'ski-stick' Cu/CuSO₄ electrodes, and utilise a cable connection to a test point facility on the pipeline. Mobile units can be provided with long lengths of light-gauge insulated wire to provide the contact between the data logger and the test point, and to provide a calibrated distance measurement, with an accuracy normally better than $\pm 0.1\%$ ². The most sophisticated data loggers are capable of time synchronisation with additional units, which can be used either for static potential measurements at chosen locations or for 'switching' the impressed-current power sources in the 'ON'/'OFF' mode. The synchronisation may be by radio link or hard wire and it is possible to provide an accuracy of synchronisation between all units of ± 1 ms over a 12 h period. Thus, overall, the mobile data logger combines pipe/soil potential measurement, distance and synchronised time together with any codes added to record geographic or topographic features.

For potential surveys on offshore platforms it is necessary to locate numerous reference electrodes at all levels on the structure. The hard-wire connections from these electrodes together with, for example, similar connections from specially monitored sacrificial anodes are best terminated and displayed at the surface on 'mimic' display monitoring panels.

Monitoring offshore potentials remotely, can now be undertaken on offshore platforms and pipelines by the use of acoustics, thus minimising the need to rely on vulnerable cabling³. The installation comprises remote monitoring units which may be interrogated by a surface unit. The monitoring unit may be provided with two reference electrodes, one zinc, one Ag/AgCl, connected to an electronic circuit, comprising two comparators, an encoder and a battery powered transmitter, capable of emitting acoustic pulses into the surrounding seawater over an approximate ten-year service-life. The structure connection is made through the watertight housing of the unit which becomes electrically common to the structure on installation. The surface unit which may be located on the platform or in a boat, is used in conjunction with a surface transducer immersed in the sea to receive the acoustic pulses transmitted by the monitoring unit. The structure potential information is decoded for presentation on a digital display.

It would normally be necessary to locate more than one monitoring unit on a structure. Thus each unit will only transmit its information on receiving coded instructions. Surface units can commonly accommodate up to 80 different codes. The ability to interrogate and receive over any distance is dependent upon the acoustic operation frequency. Relatively high frequencies are preferable, as they avoid problems of pulse reverberations and echoes from structural members. Typically data can be transferred over a distance of 2 km. This type of acoustic unit gives accuracies in potential measurement of ± 10 mV.

For offshore pipelines, continuous potential profile surveys have employed normal reference electrodes mounted in a 'tow-fish' designed for streamlined towing from a boat travelling along the line of the pipeline. Connection to the pipeline is maintained by means of a light-gauge PVC coated copper wire, and a continuous potential is recorded, along with the length of wire dispensed and position coordinates. Moving at a velocity of 3–4 m/s the tow-fish carries the reference electrode at a uniform depth. Typically, however, the reference cell is maintained between 5 and 30 m from the pipe. The effect of high relative velocities, pressure, oxygen content and other environmental parameters on the stability of the reference electrodes is still uncertain.

Current Density Devices

The measurement of current densities in the vicinity of a cathodically protected structure is a comparatively new principle used chiefly to monitor the effectiveness of offshore protection systems. These measurements are undertaken by twin half-cell devices either installed for stationary use or moved about the structure by diver or remote controlled vehicle.

The voltage drop required to be measured in seawater to provide current density levels will inevitably be small, and therefore the difference between the two reference electrodes should also be as small and as constant as possible. A current density sensor designed to overcome this possible source of error utilises two zinc reference electrodes fixed to a rotating shaft^{4,5}. The zinc electrodes are shielded from water flow by porous material in order to reduce the tendency to fluctuations in the potentials of the electrodes. The sensor assembly provides two signals which are separated by a filter: a sine signal produced by the cell rotation and the signal due to the difference between the potentials of the two cells. Both these signals are amplified and recorded at the surface. Utilising computerised finite difference analysis, information may then be obtained on anode current outputs, predicted anode life and the presence of defects in the structure coating.

Associated Instruments

Buried pipeline coating survey instruments are now available which, by measurement of the electromagnetic field radiating from a pipeline created by an applied a.c. signal, are able to compute the attenuation of the signal in dB/km or mB/m and so provide an assessment of pipeline coating quality⁶. The signal generator typically operates at a frequency of approximately

1 000 Hz for thick coatings such as reinforced coal tar enamel, being selected to minimise interference from commonly occurring frequencies while maximising the distance the signal will travel, some 5–10 km on a reasonably well-coated pipeline. For thin film, coatings, such as a fusion-bonded epoxy, a frequency of 200 Hz has been found more appropriate.

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10.8 Anodic Protection

Fontana and Greene¹ state that 'anodic protection can be classed as one of the most significant advances in the entire history of corrosion science', but point out that its adoption in corrosion engineering practice is likely to be slow. Anodic protection may be described as a method of reducing the corrosion rate of immersed metals and alloys by controlled anodic polarisation, which induces passivity. Therefore, it can be applied only to those metals and alloys that show passivity when in contact with an appropriate electrolyte. This decrease in corrosion increases the life of components/plant as well as reducing the contamination of the liquid, so is particularly beneficial in the manufacture, storage and transport of chemicals such as acids. Edeleanu first demonstrated the feasibility of anodic protection and also tested it on small-scale stainless-steel boilers used for sulphuric acid solutions²⁻³. This was probably the first industrial application, although other experimental work had been carried out elsewhere⁴⁻⁵. Fortunately electrochemical tests in the laboratory can give an accurate assessment of the corrosion behaviour, and the operating parameters for a specific anodic protection system can be obtained.

Principles

Before considering the principles of this method, it is useful to distinguish between anodic protection and cathodic protection (when the latter is produced by an external e.m.f.). Both these techniques, which may be used to reduce the corrosion of metals in contact with electrolytes, depend upon the electrochemical mechanisms that result from changing the potential of a metal. The appropriate potential-pH diagram for the Fe-H₂O system (Section 1.4) indicates the magnitude and direction of the changes in the potential of iron immersed in water (pH about 7) necessary to make it either passive or immune; in the former case the stability of the metal depends on the formation of a protective film of metal oxide (passivation), whereas in the latter the metal itself is thermodynamically stable and egress of metal ions from the lattice into the solution is thus prevented.

A further difference is that in anodic protection the corrosion rate (passivation current density) will always be finite, whereas ideally a completely cathodically protected metal should not corrode at all. Raising the potential

of an anodically protected metal may actually increase the corrosion rate if the metal exhibits transpassivity, whereas depressing the potential of a metal far below the protective potential will not affect the corrosion rate although it will be wasteful in terms of power consumption. Nevertheless it should be noted that a too negative potential can be detrimental in certain cases (see Section 10.1). Hence over- or under-protection can cause catastrophic increases in the corrosion rates, thus Palmer⁶ suggested that 'passivation is tricky'. In anodic protection the article to be protected is made the anode in an electrochemical circuit with an appropriate cathode such as mild steel, stainless steel or oxidised graphite. The potential of the anode is maintained in the passive region by a potentiostat using a suitable reference electrode.

The significance of the Flade⁷ potential E_F , passivation potential E_{pp} , critical current density $i_{crit.}$, passive current density, etc. have been considered in some detail in Sections 1.4 and 1.5 and will not therefore be considered in the present section. It is sufficient to note that in order to produce passivation (a) the critical current density must be exceeded and (b) the potential must then be maintained in the passive region and not allowed to fall into the active region or rise into the transpassive region. It follows that although a high current density may be required to cause passivation ($> i_{crit.}$) only a small current density is required to maintain it, and that in the passive region the corrosion rate corresponds to the passive current density ($i_{pass.}$).

Passivity of Metals

Since anodic protection is intimately related to passivity of metals it is relevant to review certain aspects of the latter, before considering the practical aspects of the former. The relative tendency for passivation depends upon both the metal and the electrolyte; thus in a given electrolyte, titanium passivates more readily than iron, and Fe-18Cr-10Ni-3Mo steel passivates more readily than Fe-17Cr steel. The ability to sustain passivity increases as the current density to maintain passivity ($i_{pass.}$) decreases, and as the total film resistance increases, as indicated for metals and alloys in 67 wt.% sulphuric acid (Table 10.30)⁸. The lower the potential at which a passive metal becomes active (i.e. the lower the Flade potential) the greater the stability of passivity, and the following are some typical values of E_F (V):

Table 10.30 Current density to maintain passivity and film resistance of some metals and alloys in 67 wt% sulphuric acid (after Shock, Riggs and Sudbury⁸)

<i>Metal or alloy</i>	<i>Current density to maintain passivity</i> ($i_{pass.}$, $A m^{-2}$)	<i>Total film resistance</i> (Ωcm)
Mild steel	1.5×10^{-1}	2.6×10^4
Stainless steel (Fe-18Cr-8Ni)	2.2×10^{-2}	5.0×10^5
Stainless steel (Fe-24Cr-20Ni)	5×10^{-3}	2.1×10^6
Stainless steel (Fe-18Cr-10Ni-2Mo)	1×10^{-3}	1.75×10^7
Titanium	8×10^{-4}	1.75×10^7
Carpenter 20 (Fe-25Cr-20Ni-2.5Mo-3.5Cu)	3×10^{-4}	4.6×10^7

titanium -0.24 , chromium -0.22 , steel $+0.10$, nickel $+0.36$ and iron $+0.58^9$. These values are only approximate, since they depend upon the experimental conditions such as the pH of the solution¹⁰. The Flade potential is given by

$$E_F = E_F^\circ - n0.059 \text{ pH}$$

where E_F° = the standard Flade potential at pH = 0, and

n = a number between 1 and 2 depending upon the metal and its condition.

Table 10.30 gives the current density to maintain passivity of certain metals and also the total film resistance. Only those metals which have a Flade potential below the standard reversible hydrogen potential (0.00 V at $a_{\text{H}^+} = 1$) can be passivated by non-oxidising acids, e.g. titanium can be passivated by hydrogen ions which are sufficiently oxidising, whereas mild steel requires an oxidising agent with the power of fuming HNO_3 .

The addition of a more passive metal to a less passive metal normally increases the ease of passivation and lowers the Flade potential, as in the alloying of iron and chromium in 10 wt. % sulphuric acid (Table 10.31)⁹. Tramp copper levels in carbon steels have been found to reduce the corrosion in sulphuric acid. Similarly 0.1% palladium in titanium was beneficial in protecting crevices¹², but the alloy dissolved much faster than commercial grade titanium when both were anodically protected. The addition of 2% nickel in titanium has also improved the resistance to intense local attack

Table 10.31 Effect on critical current density and Flade potential of chromium content for iron-chromium alloys in 10 wt. % sulphuric acid (after West⁹)

Chromium (%)	Critical current density ($i_{\text{crit.}}$, Am^{-2})	Flade potential (E_F , V)
0	1.0×10^4	+0.58
2.8	3.6×10^3	+0.58
6.7	3.4×10^3	+0.35
9.5	2.7×10^2	+0.15
14.0	1.9×10^2	-0.03

Table 10.32 Effect on critical current density and passivation potential on alloying nickel with chromium in 1N and 10N H_2SO_4 both containing 0.5N K_2SO_4 (after Myers, Beck and Fontana¹¹)

Nickel (%)	Critical current density ($i_{\text{crit.}}$, Am^{-2})		Passivation potential (E_{pp} , V)	
	1N acid	10N acid	1N acid	10N acid
100	1.0×10^3	2.3×10^2	+0.36	+0.47
91	9.5	3.9×10	+0.06	+0.14
77	1.1	8.2	+0.07	+0.08
49	2×10^{-1}	2.0	+0.03	+0.06
27	1.2×10^{-1}	4.1×10^{-1}	+0.02	+0.05
10	1.3×10^{-2}	1.1×10^{-1}	+0.04	+0.08
1	1.0×10	5.0×10	-0.32	-0.20
0	1.5×10	8.0×10	-0.30	-0.20

Table 10.33 Critical current density and current density to maintain passivity of stainless steel (Fe-18 to 20Cr-8 to 12Ni) in different electrolytes (after Shock, Riggs and Sudbury⁸)

<i>Electrolyte</i>	<i>Critical current density</i> ($i_{crit.}$, Am^{-2})	<i>Current density to maintain passivity</i> ($i_{pass.}$, Am^{-2})
20% sodium hydroxide	4.65×10	9.9×10^{-2}
67% sulphuric acid (24°C)	5.1	9.3×10^{-4}
Lithium hydroxide (pH = 9.5)	8.0×10^{-1}	2.2×10^{-4}
80% nitric acid (24°C)	2.5×10^{-2}	3.1×10^{-4}
115% phosphoric acid (24°C)	1.5×10^{-4}	1.5×10^{-6}

Table 10.34 Effect of concentration of sulphuric acid at 24°C on corrosion rate and critical current density of stainless steel (after Sudbury, Riggs and Shock¹⁴)

<i>Sulphuric acid (%)</i>	<i>Corrosion rate</i> ($\text{gm}^{-2} \text{d}^{-1}$)	<i>Critical current density</i> ($i_{crit.}$, Am^{-2})
0	0	47
40	48	16
45	120	14
55	192	10
65	168	7
75	144	4
105	0	1

in neutral and alkaline solutions¹³. Since exceptions may exist, each system should be considered separately, as indicated by the fact that both the additions of nickel to chromium and also chromium to nickel decrease the critical current density in a mixture of sulphuric acid and 0.5 N K_2SO_4 (Table 10.32)¹¹.

These parameters depend upon the composition, concentration, purity, temperature and agitation of the electrolyte. The current densities, required to obtain passivity $i_{crit.}$ and to maintain passivity $i_{pass.}$ for a 304 stainless steel (Fe-18 to 20Cr-8 to 12Ni) in different electrolytes, are given in Table 10.33⁸. From the data in this table, it can be seen that it is about 100 000 times easier to passivate instantaneously large areas of this steel in contact with 115% orthophosphoric acid than in 20% sodium hydroxide. The concentration of the electrolyte is also important and for a 316 stainless steel (Fe-16 to 18Cr-10 to 14Ni-2 to 3Mo) in sulphuric acid, although there is a maximum corrosion rate at about 55%, the critical current density decreases progressively as the concentration of acid increases (Table 10.34)¹⁴. When the optimum conditions are used for anodic protection the rate of corrosion can be reduced to an acceptable value¹⁵. Thus for 40% nitric acid the rate of corrosion of mild steel was approximately 10^5 mm y^{-1} , but with anodic protection it fell to less than 20 mm y^{-1} . The presence of impurities, particularly halogen ions, that retard the formation of a passive film, is often detrimental as illustrated by the fact that the addition of 3.2% hydrochloric acid to 67% sulphuric acid raises the critical current density for the passivation of a 316 stainless steel¹⁶ from 5 to 400 Am^{-2} and the current density to maintain passivity from 0.001 to 0.6 Am^{-2} . This is potentially dangerous,

and the effect of the chloride ion on the passivation of iron has been studied by Pourbaix¹⁷ who has produced a modified potential-pH diagram for the Fe-H₂O system. Therefore, the use of the calomel electrode in anodic-protection systems is not recommended because of the possible leakage of chloride ions into the electrolyte, and metal/metal oxide^{18,19} and other electrodes^{20,21} are often preferred. Because of this chloride effect the storage of hydrochloric acid requires a more passive metal than mild steel, and titanium anodically protected by an external source of current or galvanic coupling has been reported to be satisfactory^{22,23} although even this oxide film has sometimes been found to be unstable²⁴. Other additions, such as chromous chloride to chromic chloride, may result in the breakdown of passivity on titanium, but fortunately in this application, anodic protection gives repassivation and increases the corrosion resistance in the new solution by a factor of thirty²⁵.

An increase in the temperature of an electrolyte may have several effects: it may make passivation more difficult, reduce the potential range in which a metal is passive and increase the current density or corrosion rate during passivity as indicated in Fig. 10.54 for mild steel in 10% H₂SO₄. These changes are illustrated for several steels in different acids in Table 10.35²⁶ and it may be noted that, whereas the critical current density for the 316 steel increases with the temperature of the sulphuric acid, the opposite effect is observed with the 304 steel. During the storage of an acid, changes in the ambient temperature between day and night or summer and winter may double the current required for protection, and the increase may be even higher during manufacture or heat-transfer processes, so these should be considered at the design stage. Agitation or stirring of an electrolyte in

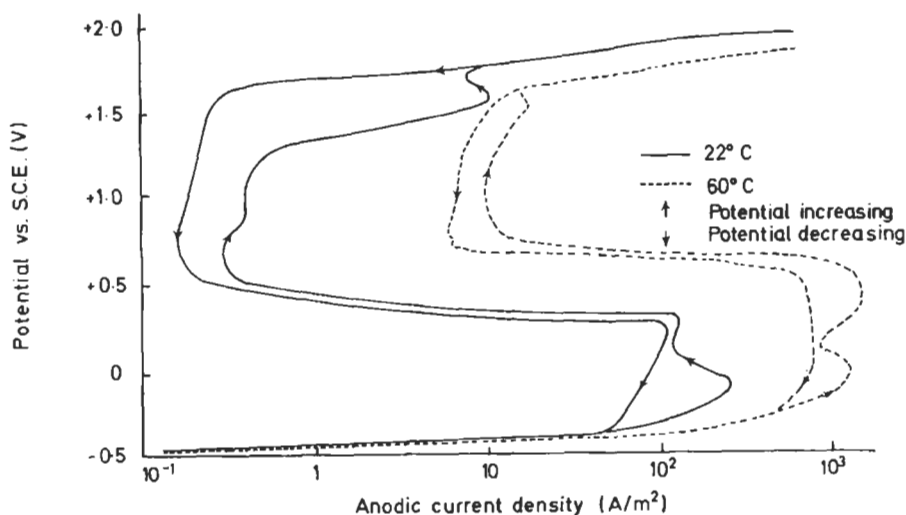


Fig. 10.54 Potentiostatic anodic polarisation curves for mild steel in 10% sulphuric acid. Note the magnitude of the critical current density which is 10^2 – 10^3 A/m²; this creates a problem in practical anodic protection since very high currents are required to exceed i_{crit} , and therefore to passivate the mild steel

Table 10.35 Effect of temperature on different acids on the operating variables for anodic protection of different steels (after Walker and Ward²⁶)

Alloy	Acid concentration	Temp. (°C)	Critical current density	Current density to maintain passivity	Corrosion rate (mm y ⁻¹)		Passive potential range (V)
			(<i>i</i> _{crit.} , Am ⁻²)	(<i>i</i> _{pass.} , Am ⁻²)	Unprotected	Anodically protected	
Stainless steel 304 ⁸ (Fe-18 to 20Cr- 8 to 12Ni)	Phosphoric, 115%	24	1.5 × 10 ⁻⁴	1.5 × 10 ⁻⁶			
		82	3.1 × 10 ⁻⁴	1.5 × 10 ⁻⁶			
		177	6.5 × 10 ⁻¹	2.2 × 10 ⁻²			
	Nitric, 80%	24	2.5 × 10 ⁻²	3.1 × 10 ⁻⁴			
		82	1.2 × 10 ⁻¹	1.1 × 10 ⁻³			
	Sulphuric, 67%	24	5.1	9.3 × 10 ⁻⁴			
82		4.6 × 10 ⁻²	2.9 × 10 ⁻³				
Stainless steel 316 (Fe-16 to 18Cr- 10 to 14Ni-2 to 3Mo)	Sulphuric, 67%	24	5.0	1 × 10 ⁻³			0.26-1.09
		66	4.0 × 10 ¹	3 × 10 ⁻³			0.27-1.04
		93	1.1 × 10 ²	9 × 10 ⁻³			0.32-0.72
	Phosphoric, 115%	93					0.26-1.14
		117					0.26-0.94
	Phosphoric, 75-80%	104		9 × 10 ⁻² -1.4 × 10 ⁻¹	1.5	0.12	
		121		1.5 × 10 ⁻¹ -3.5 × 10 ⁻¹	2.2	0.12	
		135		3.8 × 10 ⁻¹ -4.4 × 10 ⁻¹	5.3	0.85	
Carbon steel ⁵⁷	Sulphuric, 96%	27		1.1 × 10 ⁻²	0.15	0.01	
		49		1.16 × 10 ⁻¹	0.8	0.11	
		93		1.16	2.8	0.8	

Table 10.36 Effect of electrolyte agitation on corrosion rate and the current density to maintain passivity of mild steel in acid solutions at 27°C (after Walker and Ward²⁶)

Acid	Condition	Corrosion rate (mm y ⁻¹)		Current density to maintain passivity (i _{pass.} , A m ⁻²)
		Unprotected	Anodically protected	
Spent alkylation acid (sulphuric acid and organic matter) ²⁷	Stirred	3.0	0.15	2.48 × 10 ⁻¹
	quiescent	1.4	0.12	3.2 × 10 ⁻²
Sulphuric acid, 93% ²⁸	Stirred	3.3	0.28	
	quiescent	0.9	0.07	

certain conditions may increase the rate of corrosion of immersed metals and raise the passivation current density^{27,28} (Table 10.36)²⁶. Finley and Myers have found that both the temperature of the electrolyte²⁹ and cold working of the metal³⁰ have a marked effect on the anodic polarisation of iron in sulphuric acid.

Because these variables have a very pronounced effect on the current density required to produce and also maintain passivity, it is necessary to know the exact operating conditions of the electrolyte before designing a system of anodic protection. In the paper and pulp industry a current of 4 000 A was required for 3 min to passivate the steel surfaces: after passivation with thiosulphates etc. in the black liquor the current was reduced to 2 700 A for 12 min and then only 600 A was necessary for the remainder of the process³¹. From an economic aspect, it is normal, in the first instance, to consider anodically protecting a cheap metal or alloy, such as mild steel. If this is not satisfactory, the alloying of mild steel with a small percentage of a more passive metal, such as chromium, molybdenum or nickel, may decrease both the critical and passivation current densities to a sufficiently low value. It is fortunate that the effect of these alloying additions can be determined by laboratory experiments before application on an industrial scale is undertaken.

Practical Aspects

It is essential that the throwing power of the system (the ability for the applied current to reach the required value over long distances) is good and that the potential of the whole of the protected surface is maintained in the passive region. This can normally be achieved with commercial potentiostats, providing the range of the potential over which the metal or alloy exhibits passivity is greater than 50 mV. In the case of stainless steels the corrosion rate will increase if the potential rises into the transpassive zone (or if it falls into the active zone). However, titanium does not show transpassivity and, therefore, has a large potential range over which it is passive.

In general, a uniform distribution of potential over a regular-shaped passivated surface can be readily obtained by anodic protection. It is much more difficult to protect surface irregularities, such as the recessions around sharp slots, grooves or crevices³²⁻³⁸ since the required current density will not be

obtained in these areas; therefore, a local cell is set up and corrosion occurs within the recess. This incomplete passivation can have catastrophic consequences, in the form of intergranular corrosion³⁹, stress-corrosion cracking^{40,41}, corrosion fatigue³³ or pitting^{40,42,43}. Calculations have been made of the variation of potential and current distribution down anodically protected narrow passages, and these are important because they may result in local intense pitting⁴⁴. The distribution of current and potential as well as the electrochemical and design parameters for anodic protection systems have been discussed elsewhere⁴⁵⁻⁴⁷. Stress corrosion cracking of welded structural steel containing alkali-aluminate solutions was a problem at the Bayer plant but was overcome by anodic protection⁴⁸. This difficulty can be overcome by designing the surface to avoid these irregularities around bolt and rivet holes, threaded pipe sections and imperfect welds, or by using a metal or alloy which is very easily passivated having as low a critical current density as possible. In the rayon industry, crevice corrosion in titanium has been overcome by alloying it with 0.1% palladium¹².

The throwing power of a system is particularly important in the anodic protection of pipelines and, therefore, has been widely studied^{41,49-52}. The length of the pipe that can be protected by a single cathode placed at one end depends upon the metal, electrolyte and the pipe diameter; the larger the diameter the longer the length that can be protected. Thus, for mild steel in 93% sulphuric acid the length protected (or made passive) is 2.9 m for 0.025 m diameter, 4.8 m for 0.05 m diameter and possibly about 9 m for 0.15 m diameter, whereas for mild steel in a nitrogen fertiliser (a less aggressive medium than sulphuric acid) the protected length can be as much as 60 m with one cathode. As a result of recent field tests with an 0.30 m diameter carbon-steel pipe and 93% sulphuric acid at ambient temperatures, it is proposed to install anodic-protection systems for 650 m of pipeline⁵³.

The actual passivation of a surface is very rapid, if the applied current density is greater than the critical value. However, because of the high current requirements, it has been found to be neither technically nor economically practical to consider initially passivating the whole surface of a large vessel at the same time. This can be illustrated by the fact that for a storage vessel with an area of 1 000 m² a current of 5 000 A is necessary for some metal-environment systems, so it is therefore essential to use some other technique to avoid these very high currents. It may be possible to lower the temperature of the electrolyte to reduce the critical current density before passivating the metal. The feasibility of this is indicated from the values given for some acids in Table 10.35, but generally the reduction in the total current obtained by this method is insufficient. If a vessel has a very small floor area, it may be treated in a stepwise manner^{34,50} by passivating the base, then the lower areas of the walls and finally the upper areas of the walls, but this technique is not practical for very large storage tanks with a considerable floor area. A carbon steel carbonation tower, 18 m high and diameter 2.2 m with 80 plug-in heat exchangers, for the production of ammonium hydrogen carbonate has been satisfactorily passivated by this method⁵⁴. This was necessary because the critical current density was high, 280-480 A m⁻². With protection the corrosion rate decreased to less than 0.05 mm y⁻¹.

Another method which has been successful is to passivate the metal by

using a solution with a low critical current density (such as phosphoric acid), which is then replaced with the more aggressive acid (such as sulphuric acid) that has to be contained in the vessel (see Table 10.33). Tsinman *et al.*⁵⁵ passivated a large tank of 10 000 m³ capacity (12 m high and 33.4 m internal diameter) with a dilute solution of ammonia and then gradually increased the concentration to 25%. This was necessary because the 25% solution was much more corrosive and required a much higher current to passivate than was available. The critical current density can be minimised by pretreating the metal surface with a passivating inhibitor; for example, chromate solution has been applied to the floor and lower walls of a carbon-steel storage tank, which was then used to contain 37% nitrogen fertiliser solution⁵³.

Applications and Economic Considerations

The majority of the applications of anodic protection involve the manufacture, storage and transport of sulphuric acid, more of which is produced world-wide than any other chemical. Oleum is 100% sulphuric acid containing additional dissolved sulphur trioxide. The corrosion rate of steel in 77–100% sulphuric acid is 500–1 000 $\mu\text{m y}^{-1}$ at 24°C and up to 5 000 $\mu\text{m y}^{-1}$ at 100°C which indicates the necessity for additional protection.

Anodic protection can be applied to metals and alloys in mild electrolytes as well as in very corrosive environments, including strong acids and alkalis, in which cathodic protection is not normally suitable. The operating conditions, Flade potential, critical and passive current densities can be accurately determined by laboratory experiments and the current density during passivity is often a direct measure of the actual rate of corrosion in practice. The very low corrosion rate of a passive metal or alloy results in very little metal pick-up and solution contamination or discoloration. Corrosion of unprotected steel in sulphuric acid can give an iron concentration of 5–20 ppm per day. Hence, it is almost impossible to produce electrolytic grade sulphuric acid in bare or unprotected steel, because this grade should not contain more than 50 ppm iron. In general a higher purity chemical commands a higher price. However, special care should be taken in the selection of the metal or alloy and in the design if there is a possibility of crevice or intergranular corrosion. A portable form of anodic protection is available that can be applied to rail and road tankers^{41, 56–59}. It can also be used for old vessels as well as new, so that a container designed for one liquid can be protected and used to hold a more corrosive solution. Because a system with a good throwing power can be designed, anodic-protection systems have been applied to pipelines⁵³ and spiral heat exchangers^{12, 41}. It has been found possible to maintain protection of the vapour space above a liquid, once it has been completely immersed and passivated⁴¹, and this is particularly important when the liquid level may rise and fall during storage and use.

One consequence of reducing the rate of corrosion of steel in an acid is to decrease the formation of hydrogen, which has been reported as the cause of explosions in phosphoric acid systems⁵⁹. Hydrogen may also form

Table 10.37 Summary of anodic protection application (after N.A.C.E.⁶⁶)

<i>Application</i>	<i>Vessel metal</i>	<i>Temperature range (°C)</i>	<i>Vessel type and purpose</i>	<i>Vessel size range ‡ (m)</i>	<i>Number of systems</i>	<i>Type of controller</i>	<i>Power supply size range (kW)</i>	<i>Date of first installation</i>
Oleum	Mild steel	≥50	Storage*	8D × 6H– 12D × 6H	4	On-off and proportional	0.5–5.0	Oct. 1960
100% H ₂ SO ₄	Mild steel	≥50	Storage*	4D × 4H	1	On-off	0.5	March 1960
99% H ₂ SO ₄	Mild steel	≥50	Storage*	2D × 9L– 9D × 10H	5	On-off	2.5–5.0	Nov. 1962
98% H ₂ SO ₄	Cast iron	≥93	Mix tank*†	3D × 2D	1	On-off	1.0	Aug. 1964
98% H ₂ SO ₄	Mild Steel	≥50	Storage*	8D × 6H– 9D × 9H	2	On-off	2.5	Sept. 1963
96% H ₂ SO ₄	Mild steel	≥50	Storage*	4D × 6H	2	On-off	1.0–2.5	Dec. 1961
93% H ₂ SO ₄	Mild steel	≥50	Storage	2D × 5L– 15D × 7H	14	On-off	0.5–5.0	Oct. 1962
93% H ₂ SO ₄	304 stainless steel	≥66	Heat exchanger*†	61 m ²		Proportional	1.0	Sept. 1966§
60° Bé H ₂ SO ₄	Mild steel	≥66	Storage*	8D × 6H– 12D × 6H	3	On-off	5.0	June 1965
60° Bé H ₂ SO ₄	430 stainless steel	≥50	Storage*	2D × 10L	1	On-off	0.5	June 1965

Table 10.37 (continued)

<i>Application</i>	<i>Vessel metal</i>	<i>Temperature range (°C)</i>	<i>Vessel type and purpose</i>	<i>Vessel size range ‡ (m)</i>	<i>Number of systems</i>	<i>Type of controller</i>	<i>Power supply size range (kW)</i>	<i>Date of first installation</i>
Black and spent H ₂ SO ₄	Mild steel	≥60	Storage*	4D × 6L–12D × 12H	6	On-off and proportional	2·5–10·0	Nov. 1962¶
Black H ₂ SO ₄	304 stainless steel	≥163	Storage*	3D × 3H	1	Proportional	5·0	Oct. 1966
75% H ₃ PO ₄	304 stainless steel	≥50	Storage*	24D × 10H	1	Proportional	5·0	Sept. 1963
N ₂ fertiliser solutions	Mild steel	≥50	Storage*†	30D × 5H–27D × 12H	7	On-off	5·0	Dec. 1963
Kraft cooking liquor in digester	Mild steel	≥177	Reactor*	3D × 14H	1	Time	30	1961
ClO ₂ bleach	317 stainless steel	≥60	Washer wires*	Not applicable	1	Proportional	2·5	Nov. 1963

* Chemical purity of product.

† Corrosion control of vessel.

‡ D = diameter, H = height.

§ Exchangers failed after two weeks operation due to high chloride content of cooling water, causing stress-corrosion cracking of 304 stainless steel.

¶ One application failed due to unanticipated composition variations. Relatively low unprotected rate did not provide incentive for further work.

|| There are both successful and unsuccessful pulp digester installations.

blisters at inclusions in the metal surface and can also produce grooving on vertical surfaces. Anodic protection, which has been found to reduce⁶⁰ the formation of hydrogen by 97%, can therefore prevent this effects.

The limitations of anodic protection arise from the inability to form a stable, continuous, protective, passive film on the metal to be protected. Thus metals and alloys which neither form passive films nor non-conducting solutions cannot be used. For strongly aggressive acids, such as hydrochloric acid, a very stable anode film is required and, while steel is not satisfactory, titanium^{22,61} may be suitable. The performance of titanium in strongly aggressive conditions can be improved by anodic protection, the use of inhibitors and by alloying elements⁶². The stable oxide film on protected titanium is particularly useful for reactor tanks for electroless nickel deposition. In these solutions, based on nickel sulphate and hypophosphate, no nickel plating occurs on the tank walls and there is no self-decomposition of the hypophosphate. Because of the high throwing power a single cathode can be used to protect large tanks^{63,64}. A power failure may be a considerable danger, since it can result in a drop in potential from the passive region to the active region with a considerable increase in the current density. Following the mechanical breakdown of the oxide layer on a 304L stainless steel in potassium hydroxide solution a current density as high as 10 A cm^{-2} has been measured⁶⁵. This failure may be rectified by the use of a 100% effective 'fail-safe' back-up current source or by the selection of a basically more corrosion-resistant alloy, which would be marginally satisfactory in an unprotected state. Table 10.37⁶⁶ gives some of the applications of anodic-protection systems which have been used in the USA. Most of these are for chemical purity and corrosion control in storage vessels and details are given of the size of the tank and the operating conditions.

Economically the installation of anodic protection is often very good. The advantages include a reduction in capital investment, lower maintenance and replacement costs and an improvement in the product quantity and value. The use of a potentiostat and its associated equipment involves a high installation cost but low operating costs, because only very small current densities are required to maintain passivity. In some circumstances the passive condition may persist for several hours after the current has been switched off. If this is the situation⁶⁷ it is possible to use a relatively inexpensive switching mechanism with one control and power-supply system to anodically protect three separate tanks, and therefore reduced the high initial cost. Four storage vessels, volume 160 m^3 , containing aqueous ammonia have been protected simultaneously by one system by switching the current on for 2 min and off for 6 min⁶⁸. The rate of corrosion with this technique decreased from about 0.186 mm y^{-1} to less than 0.001 mm y^{-1} . It can be seen from Table 10.38 that it is more economical to anodically protect mild steel than to use mild steel with a p.v.c. lining or to use a more resistant and expensive metal or alloy such as aluminium or stainless steel. It is worth noting that because most of the expense of an anodic-protection system is due to the cost of the potentiostat, it is more economical per unit volume to use a larger instrument and a bigger tank.

Not only is the anodic protection of a mild-steel tank cheaper than one with a glass or phenolic lining⁷⁰, but, because the steel conducts heat, it can be used for heat exchangers, and in addition it may be more stable at high

Table 10.38 Comparison of the relative cost of protecting tanks by various methods (after Reference 18:1967)

	Cost (£m ⁻² y ⁻¹)				
	<i>Mild steel protected</i>	<i>Mild steel lined</i>	<i>Stainless steel</i>	<i>Mild steel protected</i>	<i>Aluminium</i>
Tank cost	1.70	1.70	4.57	1.70	3.5
Anodic-protection system	0.94			0.04	
P.V.C. lining		4.05			
Power	0.04			0.04	
Maintenance	0.54	0.81		0.54	
Total cost	3.22	6.56	4.57	2.32	3.5
	95 000 litre			3 800 000 litre	

temperatures for long time periods. The rate of corrosion of shell and tube heat exchangers, with 93–99% H₂SO₄ on the shell side and water on the tube side, decreased from 5–10 mm/y to 25 µm/y when anodically protected. Hence protection enabled the use of either higher temperatures and velocities⁷¹, giving better heat transfer, or thinner metal sections or smaller exchangers, all of which are financially beneficial. A further advantage is that a considerable reduction in the corrosion may increase the life of chemical plant until it becomes obsolete instead of the need for repair and replacement. In very corrosive conditions it may be necessary to use a very resistant alloy together with anodic protection, e.g. Corronel 230 was employed in the extraction of uranium using hot acidic solutions, which were too aggressive to be contained by Neoprene, Karbate and Teflon coatings⁷². The reduced rate of corrosion can also improve safety by maintaining the thickness and strength of the supporting metal as well as minimising the possibility of perforation. This is particularly important if poisonous, combustible, explosive or hot liquids are involved.

Conclusion

Although the first industrial application of anodic protection was as recent as 1954, it is now widely used, particularly in the USA and USSR. This has been made possible by the recent development of equipment capable of the control of precise potentials at high current outputs. It has been applied to protect mild-steel vessels containing sulphuric acid as large as 49 m in diameter and 15 m high, and commercial equipment is available for use with tanks of capacities from 38 000 to 7 600 000 litre⁵³. A properly designed anodic-protection system has been shown to be both effective and economically viable, but care must be taken to avoid power failure or the formation of local active-passive cells which lead to the breakdown of passivity and intense corrosion.

The extent of the interest in the application of anodic protection is

indicated in the following list of recent publications. These include the application of anodic protection to titanium in the rayon industry¹², heating coils⁷³ and chromic chloride/chromous chloride solutions²⁵, electroless nickel plating^{63,64}, hydrochloric⁷⁴ and sulphuric⁷⁵ acid and neutral and alkaline chloride solutions¹³. Different steels have been used with a wide range of solutions of fertilisers^{56,76,77}, ammonia and ammonium salts⁷⁸⁻⁸¹, bicarbonates^{54,82}, sodium⁸³ and potassium⁸⁴ hydroxides, formic⁸⁵ and nitric¹⁵ acids and alkali-aluminate⁴⁸. Protected steel has also been used in the manufacture of acrylamide⁸⁶ and electrolytic manganese dioxide⁸⁷ as well as biosewage treatment plant⁸⁸. Other work on steel for storage tanks and boiling pots⁸⁹⁻⁹² for sulphuric acid has been reported as well as heat exchangers for the acid⁹³⁻⁹⁷. Further details on the application and theory of anodic protection are given in the excellent book by Riggs and Locke⁹⁸.

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11 PRETREATMENT AND DESIGN FOR METAL FINISHING

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11.1 Surface Treatment Prior to Applying Coatings

The attainment of a clean surface prior to the application of any subsequent treatment or coating is essential, whether this subsequent operation is electroplating, anodising, chemical treatment or organic coating.

The standard of cleanliness which must be achieved has been stated to be 'that which will allow the subsequent process to be carried out satisfactorily'. As an example, the degree of cleanliness required to satisfactorily zinc plate from an acid solution is somewhat higher than that required prior to zinc plate from a high-cyanide alkali zinc solution. This should never be taken as a licence to skimp on surface preparation. However, the arguments over 'surface-tolerant' paint coatings abound and will probably continue. It is to a very large extent true that problems of early failure in metal finishing are traceable to incorrect or insufficient surface preparation.

Although many standards exist for cleaning treatments for metal surfaces, for example Defence Standard DEF STAN 03-2/1, these are often fairly general guides which in some cases may be regarded as somewhat outdated due to recent advances in treatment technology and changes in industrial practice.

In general, there are two types of surface contamination: (1) organic contamination—such as oils, greases, paint coatings etc.; and (2) inorganic contamination—such as rust, oxide films, corrosion products, scale, anodic films etc. Although these two types of contaminant can be removed simultaneously, it is simpler to consider the cases separately.

Removal of Organic Contamination

As previously stated, this consists of oils, greases, preservatives or old paint coatings which must be removed prior to further finishing. The removal of paint coatings with chemical paint strippers is outside the scope of this section, and readers are referred to specialist publications on the subject. Sources of the remaining organic contamination are cutting and machining fluids, preservatives, tramp oils from, for example, rolling operations, press lubricants and mechanical or manual handling operations.

Four means of soil removal have been proposed: mechanical action;

solvency; detergency; and chemical reaction. In all cleaning operations one or more of these mechanisms will contribute more or less to the overall cleaning procedure, dependent upon the cleaning method and solution employed.

Virtually 100% mechanical action is employed in abrasive blast cleaning. With chemical cleaning, performance will be enhanced by the use of mechanical action, such as brushing, air agitation, spraying, electrolysis or ultrasonics. Solvency is where the soil to be removed dissolves in the cleaning medium, for example mineral oil in chlorinated solvents. Detergency is the 'lifting' action attributed to some alkalis and to special surface-active agents—commonly referred to as surfactants or originally, 'syndets', short for 'synthetic detergents'. Chemical reaction is characterised by, for example, the saponification of some oils in strong alkali, or the reaction of rust with acid solutions.

The main types of cleaners used for the removal of organic contaminants are: solvent cleaners, neutral cleaners, acid cleaners and alkali cleaners.

Solvent Cleaning

This area can be split into four major categories of cleaner type: cold solvent, hot/vapour solvent, emulsifiable and emulsion.

Cold Solvents Solvents, for example, white spirit or paraffin, used either by immersion or by manual application are not to be recommended as effective, or particularly safe methods, of degreasing. When used by immersion, the holding tank can become heavily contaminated with soil, which will remain on the work after the solvent has evaporated. The use of solvent-soaked rags, although a time-honoured procedure, is now being frowned upon on the grounds of operator safety; aqueous based pre-wipes are available.

Vapour Degreasing The use of hot/boiling solvents, with both immersion of the articles to be cleaned in the bulk solvent and/or in the overlying vapour, using specially designed installations, is a far more effective use of solvents for cleaning purposes. A simplified diagram of a typical small installation is shown in Fig. 11.1. The solvent, which is generally of a halogenated hydrocarbon type, is held in a sump at the base, which is heated by any suitable means and under thermostatic control. Above this may be a wire mesh on which the workpieces are rested. Some way above this, there are condenser coils, often water-filled. Between the mesh and the coils, therefore, is created a region where the solvent is in vapour form. When cold workpieces are introduced, the vapour condenses on the work, the liquid solvent flows off, taking the oil with it. To a large extent, only clean solvent is vaporised, thus ensuring that only fresh solvent is used to clean the workpiece until the sump becomes overcontaminated, when the solvent must be cleaned or replaced.

Care should be exercised with some metals, notably aluminium, that solvent with free chloride is not used, as this could lead to pitting of the metal surface.

The advice of the manufacturers of the installation and the suppliers of the solvent should always be heeded in the operation of these installations

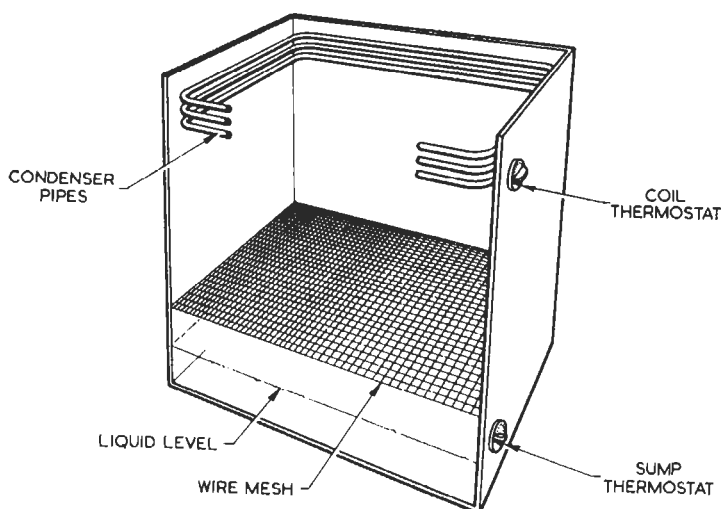


Fig. 11.1 Cut-away drawing of vapour degreasing plant

to ensure their trouble-free running. Effective fume extraction must be available above the installation and the work must be removed slowly enough to ensure that all the solvent has evaporated from the work before it leaves the extracted area. The rules governing exposure limits are frequently changed, and up-to-date advice must be sought.

Emulsifiable Cleaners (Water Rinsable Cold Solvent Cleaning) Emulsifiable cleaners (sometimes incorrectly referred to as emulsion cleaners) are blends of organic solvent, often kerosene, with surface active agents. The work is immersed in the unheated solution for a sufficient time for the cleaner to penetrate the soil thoroughly. The articles are then removed and water rinsed. Additives in the cleaner allow the solvent, with its accompanying soil, to emulsify in the water thus removing the contamination. Spray rinsing or agitation in an immersion rinse will aid removal of the residues.

The disposal of the rinse water is dependent on local effluent restrictions. In some areas, mere dilution will be required before discharge, but in others, the water may have to be stored and the emulsion broken before discharge of the water layer and approved disposal of the organic material.

As with all solvent-based materials, the need to observe TLV limits and the need for the work to be carried out only under effective fume extraction must be taken into account when considering this type of cleaning product.

The cleanliness of the surface produced by emulsifiable cleaners is rarely of a very high standard, and additional cleaning may well be necessary before further finishing operations. Success has been achieved, however, in the use of these products prior to some immersion phosphating operations, where the crystal growth can be quite refined due to the absence of the passivation effect often encountered with some heavy-duty alkali cleaners. The supplier of the phosphating solution should be asked to advise on the suitability of any particular cleaning/pretreatment combination.

Another benefit gained from the use of emulsifiable cleaners is that the surface produced is usually hydrophobic and thus, to an extent, resistant to tarnishing and corrosion in storage.

Emulsion Cleaners These are materials, containing blends of organic solvents and surfactants, which are added to water to form an emulsion. Typical concentrations are in the range 0.5–5%. Such emulsions are normally used by spray, as either a pre-clean in a multi-stage pretreatment line, or as the cleaner in an industrial washing machine. Such washing machines are often used to clean parts which are contaminated with cutting oils etc., and which require inspection before storage. Like the emulsifiable cleaners, the emulsion cleaners, after rinsing, often leave a hydrophobic surface which is resistant to short-term corrosion.

Emulsion cleaners can be used hot or cold. Heat generally improves the cleaning action but, in most cases, leads to an objectionable increase in the smell associated with solvent products.

Neutral Cleaners

These are rapidly replacing emulsion and alkali products for use in industrial washing machines. They are generally used at pH 7.5–9, considerably lower than corresponding alkali products.

Neutral cleaners have a soap-type hydrotrope base, with additions of surfactant (to improve cleaning, wetting, penetration and defoaming), inhibitors (which may be nitrite or organic) and a bactericide. The bactericide was often formaldehyde, but this is now being superseded by formaldehyde-free materials, based on quaternary ammonium salts.

Neutral cleaners provide the benefits of generally lower operating temperatures, reduced odour, easier effluent treatment and improved health and safety considerations over the alkali or emulsion products. Due to the inhibited nature of the surface produced, such products are used for interstage cleaning and prior to assembly. The surface is generally not suitable for immediate painting.

Acid Cleaners

The vast majority of acid-based cleaning products are for the removal of scale, rust and other oxide films (see Section 11.2). These products may contain solvents and surfactants to degrease and derust simultaneously.

There are, however, certain acid-based materials which can primarily be construed as cleaners. One such type of material is used in the cleaning of aluminium cans prior to treating and lacquering. Such cleaners are normally based on sulphuric or phosphoric acid, with, generally, additions of hydrofluoric acid and surfactants. These materials are sprayed on to pre-formed cans to remove the lubricant used during the can-forming operation. The fluoride is present to enhance the removal of 'fines' of metal swarf in the cans as well as to remove the oxide film.

Fluoride-free acid cleaners are finding their way into the general pretreatment cleaning of aluminium as an alternative to strong alkali materials.

Although more expensive in terms of initial make-up and plant requirements, the rate of loss through cleaning and etching can be less. Furthermore, the need for a desmut material, required after alkali etching, is obviated.

As the surface smoothing and levelling effects are somewhat limited, the use of acid cleaners prior to anodising or electropainting, where surface defects can be enhanced, is not common.

Care must be taken here not to confuse acid cleaners with the high-strength, phosphoric acid-based chemical polishes and chemical brighteners, which are used specifically to obtain the surface finish which such materials produce. Also in the category of acid cleaners could be considered the light-weight alkali-metal phosphating cleaner-coater solutions, but a discussion on such materials is best left to specialist publications on metal pretreatment chemicals.

Alkali Cleaners

This category is without doubt the largest among cleaner types. Alkali cleaners can be used before almost every conceivable metal finishing operation at one stage or another. There is a bewildering array of products available in the market place. There are alkali cleaners which can be used by spray, by immersion, by manual application or by all three, or maybe by two out of the three methods. They can come as powders or as built liquids. They may be single or multi-pack, to be used as supplied or at a range of dilutions. They may require high temperatures or work successfully at ambient temperature. They may be suitable for cleaning one metal only or have multi-metal capability. The user thus has an immense range from which to choose.

Consideration will first be given to the inorganic builders used to produce the base material. The pH values of several commonly used materials are shown in Table 11.1. Hydroxides are the simplest, strongest alkalis and most commonly used. A major effect of hydroxides in cleaning is saponification: the conversion of certain oils and greases to water-soluble soap-type materials. Hydroxides also produce solutions of high conductivity, as required for electrocleaning.

Beside the benefits of hydroxides must be placed certain disadvantages:

1. The possible passivation of iron and steel surfaces; this can be a problem prior to chemical conversion coatings.

Table 11.1 pH values of certain alkalis as 1% w/v solution at 50°C

<i>Alkali</i>	<i>pH</i>
NaOH	12.7
Na ₂ CO ₃	11.3
Na ₂ SiO ₃	12.2
Na ₃ PO ₄	11.8
Na ₂ P ₂ O ₇	10.6
Na ₅ P ₃ O ₁₀	9.8
Na ₂ B ₄ O ₇	9.3
NaC ₇ H ₁₃ O ₈	7.8

2. The soaps produced by saponification may give excessive foam during spray cleaning or react with hard-water salts to form scum and scale.
3. Light metals, such as zinc and aluminium, can be attacked more than is desirable.
4. Powder products formulated with too much hydroxide can be hygroscopic and thus tend to go solid in storage rather than remaining as free-flowing powders.
5. Spray cleaners based on hydroxide can pick up carbon dioxide from the atmosphere, and such carbonated solutions become less effective.

Carbonates and bicarbonates are used as lower alkalinity adjuncts or substitutes for hydroxide. It has been suggested that hydroxide/carbonate systems are more resistant to carbonation during spraying than hydroxide-only solutions. Powder products blended with light sodium carbonate are much less hygroscopic, and the carbonate can be a useful 'carrier' for liquid additives, such as surfactants and solvents.

Silicates can offer an almost complete cleaning system on their own. Sodium metasilicate, the most commonly used of these materials, has a high enough pH value to cause saponification, and the structure of the polysilicate anion formed gives degrees of detergency, peptisation and inhibition. Thus, silicates are often found in multi-metal cleaners. Light metals, such as zinc and aluminium will not be attacked if the silicate level is sufficiently high and the free caustic level sufficiently low.

Cleaners containing silicate can cause problems. They should not be used prior to an alkaline process on aluminium, owing to the formation on the surface of alkali-insoluble aluminium silicate. Silicated cleaners can also cause problems before some surface-sensitive zinc phosphating solutions, especially the more modern low-zinc type.

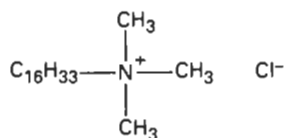
Phosphates are another common ingredient of alkali cleaners. They have both detergent and peptisation properties. The pyro- and polyphosphates in particular have water softening capabilities.

Borates are often the base for light-duty cleaners associated with the cleaning of light metals, due to their inhibiting action and mild pH. They can also be used, to a certain extent, as a substitute for phosphates when a phosphate-free product is required.

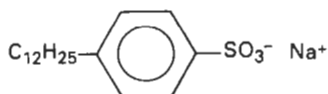
The organic acid salts, such as EDTA and heptonate, are included for water softening properties, and to assist in the removal of solid particles. Gluconate and heptonate, in particular, are effective in the highly alkaline solutions used for etching aluminium and prevent the precipitation of aluminium hydroxide scale and sludge.

Surfactants are probably the materials which most affect the performance of alkali cleaners. Surfactants are complex chemicals which modify the solubility of various materials in, and their surface affinity for, oil and water. The diverse composite which makes up the surface of a metal object must be fully wetted out if the cleaner is to perform properly. Surfactants lower the surface tension to allow wetting out to occur. Oils and greases must either be dissolved off the surface or lifted from it; surfactants assist in both areas.

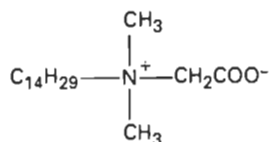
There are four broad categories of surfactant, dependent on the charge associated with the active part of the molecule:



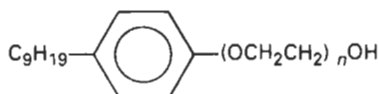
Cetyl trimethyl ammonium chloride (cationic)



Sodium dodecyl benzene sulphonate (anionic)



Myristyl dimethyl betaine (amphoteric)



Polyethoxylated nonyl phenol (non-ionic)

Fig. 11.2 Typical surfactants

1. *cationic*, where the residual charge is positive;
2. *anionic*, where the residual charge is negative;
3. *amphoteric*, where there exists both positive and negative charge centres;
4. *non-ionic*, where there is no residual charge.

Typical examples are given in Fig. 11.2.

It is the job of the formulating chemist to invent a blend from amongst all of the foregoing materials to produce a cleaner suitable for use in a particular application.

Care must be taken with some surfactant-containing cleaners not to exceed certain temperature and concentration limits. It is an old adage that a cleaning solution can be improved by making it hotter and stronger. This remains generally true, but with some surfactant-containing cleaners there are restrictions. Many commonly used surfactants have limited solubility in alkali. They become less soluble as the alkalinity, ionic strength and temperature rise. A point can, therefore, be reached when the surfactants come out of solution and, in immersion cleaning especially, performance will suffer drastically. Similarly, some spray cleaners are designed to work above a

Table 11.2 Typical alkali cleaners

<i>Constituent</i>		<i>Composition (%)</i>				
NaOH	20	60	20	0	0	
Na ₂ SiO ₃	50	20	40	60	0	
Na ₂ CO ₃ /NaHCO ₃	20	10	20	10	20	
Na ₃ PO ₄	—	—	12	20	20	
EDTANa ₄	5	5	5	5	8	
Na ₂ B ₄ O ₇	—	—	—	—	50	
Surfactant	5	5	3	5	2	
Substrate	Steel	Steel	Zinc	Multi-metal	Aluminium	
Application	Immersion	Electrocleaning	Electrocleaning	Immersion	Spray	

certain minimum temperature and strength. In this case, a surfactant is designed to come out of solution to act as a defoamer for the system.

Examples of typical simple formulations for various types of alkali cleaners are give in Table 11.2.

Electrocleaning

As is mentioned above, a significant increase in immersion cleaning performance can be achieved by the use of an applied voltage, as in electrocleaning. Hydrogen is evolved at the cathode and oxygen at the anode. These gases act with a 'scrubbing' action, greatly enhancing the cleaning process. Where possible, work will generally be cleaned cathodically, as this results in twice as much hydrogen being evolved than oxygen. However, during cathodic cleaning any dissolved metal ions have a tendency to plate-out on the metal surface, so the work will normally be given a short anodic cycle at the end of the cleaning time to dissolve this film. Periodic reverse cathodic/anodic cycling is most commonly used for articles which are oxidised and corroded as well as oily and greasy. Alkaline products containing cyanide were commonplace for this purpose, but more recent, cyanide-free solutions are being increasingly used.

For electrocleaning, care must be taken that a cleaner of sufficiently high conductivity is used to prevent solution voltage drops and 'burning' of workpieces in high current density areas. With brass and zinc, the cleaner must not be so alkaline as to cause chemical attack of the substrate before the cleaning period is completed. High anode current densities should be avoided. Care must also be taken when electrocleaning high-strength steel alloys. Hydrogen embrittlement which can occur during cathodic cleaning must be either avoided or catered for.

Ultrasonics

Another method for introducing mechanical action into immersion cleaning is by the use of ultrasonics. Here, a high frequency vibration is imparted to the solution. At the surface to be cleaned, minute bubbles are formed and

collapsed, scrubbing off the soil. Such installations are generally quite small and used for special purposes, although the overall applicability of the system is wide.

Removal of scale and rust from mild steel

The hot rolling of steel produces a surface layer of complex oxides known as 'millscale'. It is unstable, losing adhesion upon weathering, and must be removed prior to painting if predictable paint performance is to be obtained.

In rusting, the initial corrosion product of iron is ferrous hydroxide. Reacting with oxygen and water, it forms higher oxides, mainly hydrated ferric oxide and magnetite. Rust formed in industrial or marine environments contains corrosion-promoting salts and is particularly dangerous. Rust is not considered a satisfactory base over which to paint and it too must be removed.

The possible methods of surface preparation before painting hot rolled steel are discussed in the following sections.

Weathering In aggressive environments millscale detachment is likely to be complete within a year, while in a benign atmosphere descaling has taken more than five years. Depending upon the severity of exposure, steel can rust and pit during this period. The rust may be contaminated with soluble salts, making effective protective painting difficult if not impossible. For these reasons natural weathering is no longer considered an acceptable part of surface preparation.

Manual Cleaning The term encompasses all manual and mechanical methods of cleaning other than blast-cleaning. Abrasive discs, wirebrushes, scrapers, vibratory needle guns and chipping hammers are available. Manual cleaning removes neither tightly adhering millscale nor deep-seated rust from pits. None the less, it is often used for maintenance work or for the preparation of new steelwork to be exposed in non-aggressive conditions. Manual cleaning is rarely used in conjunction with high-performance long-life systems, e.g. two-pack chemically curing coatings which require a high standard of blast cleaning.

Swedish standard SIS 055900 contains two pictorial standards for manual cleaning, St2 and St3. Both require the removal of loose millscale, surface rust and foreign matter. The second and higher standard describes the prepared and dusted surface as having a pronounced metallic sheen. The St2 preparation is described as 'a faint metallic sheen'. Both are expected to correspond with their respective coloured prints in the standard. These relate to four grades of new unpainted steel:

Grade A: the surface is covered with adherent millscale; little or no rust is visible.

Grade B: The surface has started to rust and the millscale has begun to flake.

Grade C: Most of the millscale has flaked and what remains can be scraped off; the surface has rusted but there is little pitting visible to the naked eye.

Grade D: The millscale has rusted away and considerable pitting is visible to the naked eye.

Caution should be exercised when using this standard because the colours of the print may vary from one copy to another.

Acid Pickling This does not refer to the site application of weak acid solution; such treatments are of dubious merit. Acid pickling is a factory process during which steel is immersed in hot acid, removing millscale and rust. In the 'Footner' or 'Duplex' processes the steel receives a final treatment in 2% phosphoric acid, leaving a thin phosphate coating on the warm steel surface, to which the paint should be applied immediately. Once very popular for preparing steel plate, the process has been largely superseded by blast cleaning. It is still used in the pipe industry, but finding firms to deal with ad hoc quantities of structural steel or plate is now very difficult.

Flame Cleaning Now little used as a preparatory method, flame cleaning is a process whereby an intensely hot oxyacetylene flame is played on the surface of the steel. In theory, differential expansion causes millscale to detach. In practice, there is evidence that the treatment may not remove thin, tightly adhering millscale. Also, steel less than 5 mm thick can buckle. Finally, the process can 'burn in' chemicals deposited on the surface, causing premature paint failure.

Blast cleaning To remove millscale and rust, abrasive particles are directed at high velocity against the metal surface. They may be carried by compressed air, high-pressure water, or thrown by centrifugal force from an impeller wheel. For some open blasting, e.g. maintenance work, high-pressure water without abrasives may be used although this will not remove heavy corrosion products.

Common abrasives for cleaning steel are chilled iron shot and grit, steel shot and grit, iron and copper slags. BS2451: 1963 (1988) covers chilled iron products. BS5493 deals with blast cleaning in the context of protective painting in some detail.

There are three standards controlling surface finish in common use. They are issued by the Steel Structures Painting Council (USA), the Swedish Standards Organisation and the British Standards Institution. They are roughly equivalent.

	<i>SSPC</i>	<i>BS7079</i>	<i>SIS 05 5900</i>
Light	SP7	—	Sa1
Thorough	SP6	Sa2	Sa2
Very thorough	SP10	Sa2½	Sa2½
To pure metal	SP5	Sa3	Sa3

Surface 'finish' is increasingly referred to as 'surface cleanliness'. This can be misleading because the standards refer to the appearance of the blasted steel and do not deal with chemical contamination. Site tests for assessing the level of soluble salts on freshly blast-cleaned surfaces, and which allow the semi-quantitative determination of the chlorides, soluble sulphates and soluble iron salts, are urgently needed.

Blast-cleaning produces a roughened surface and the profile of that surface is important. The size and nature of the profile is largely determined by the type and size of the abrasive used. To identify and control surface roughness, comparators are available conforming to ISO 8503/1 specifica-

tion. Type G is for use with grits and Type S with shot. The comparators are intended for visual and tactile assessment of surfaces blast-cleaned to Sa2 $\frac{1}{2}$ or Sa3 only.

G. L. HIGGINS
R. S. HULLCOOP

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Standards

1. Svensk Standard SIS 05 5900–1967, Pictorial surface preparation standards for painting steel surfaces
2. BS2451:1963 (1988), 'Chilled Iron Shot and Grit'
3. BS7079:1989, 'Preparation of steel substrates before application of paint and related products'
4. BS5493:1977, *Code of Practice* for Protective Coating of Iron and Steel Structures Against Corrosion
5. DIN 8201, 'Synthetic Mineral Solid Abrasives'

11.2 Pickling in Acid

Mechanism of Scale Removal from Steel with Acid

When mild steel is heated in air at between 575 and 1 370°C an oxide or scale forms on the steel surface. This scale consists of three well-defined layers, whose thickness and composition depend on the duration and temperature of heating. In general, the layers, from the steel base outwards, comprise a thick layer of wüstite, the composition of which approximates to the formula FeO , a layer of magnetite (Fe_3O_4), and a thin layer of haematite (Fe_2O_3).

When the steel is rapidly cooled, the thickness and composition of these layers remain more or less unchanged, but when it is slowly cooled through 575°C the scale becomes enriched in oxygen and the remaining wüstite layer breaks down to some extent into an intimate mixture of finely divided iron and magnetite¹.

Holding of the temperature between 400 and 575°C causes the iron particles to coagulate and the scale becomes further enriched in oxygen. Since wüstite is unstable below 575°C, scales produced at temperatures lower than this contain magnetite and haematite only¹. In addition, the scales are often cracked and porous. This is due to the difference in contraction

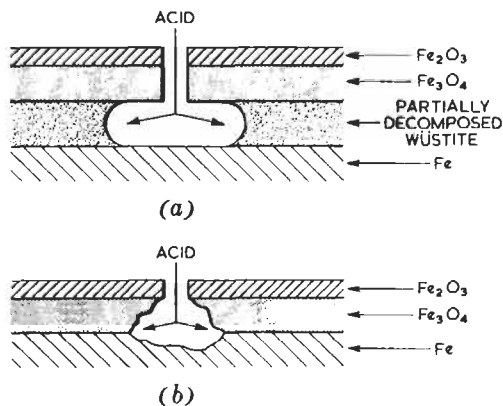


Fig. 11.3 Mechanism of scale removal with acid. (a) High-temperature scale and (b) low-temperature scale

between scale and metal on cooling and to the change in volume when the metal is oxidising.

When a steel which has been slowly cooled through 575°C is immersed in mineral acid, the acid penetrates through the cracks and pores in the upper layers of scale and rapidly attacks the decomposed wüstite layer, thus releasing the relatively insoluble magnetite and haematite layers (Fig. 11.3). This rapid dissolution of the wüstite layer is due to the setting up of many minute electrolytic cells between the finely divided iron particles, magnetite and acid. The iron, being anodic, dissolves to form ferrous ions, and the magnetite, being cathodic, is reduced, forming more ferrous ions. Since the three constituents of these cells are good electrical conductors, the resistance of the cells is so small that the rate of dissolution of the decomposed wüstite layer is largely governed by the rate at which acid diffuses through the cracks to it, and the rate at which spent acid diffuses from it. A similar but slower action occurs between the exposed metal and the magnetite and haematite layers which have not been detached².

The pickling rate of steels which have been rapidly cooled or held between 400 and 575°C is slower. This is due in the former case to the absence of the iron/magnetite cell action, and in the latter to the increased cell resistance resulting from coagulation of the iron. Similarly, the pickling rate of steels scaled at temperatures below 575°C is slow, because the resistance of the few larger cells formed between the magnetite and the base metal is high.

Apart from this cell mechanism in the scale, and between metal and scale, another cell action occurs on the exposed steel surface. In this ferrous ions are produced at the anodic areas and hydrogen at the cathodic areas.

Hydrogen Embrittlement

Although the majority of the hydrogen produced on the cathodic areas is evolved as gas and assists the removal of scale, some of it diffuses into the steel in the atomic form and can render it brittle. With hardened or high-carbon steels the brittleness may be so pronounced that cracks appear during pickling. Austenitic steels, however, are not so subject to embrittlement.

If the acid contains certain impurities such as arsenic, the arsenic raises the overvoltage for the hydrogen evolution reaction. Consequently, the amount of atomic hydrogen diffusing into the steel, and the brittleness, increase.

As well as causing brittleness, the absorbed gas combines to form molecular hydrogen on the surface of inclusions and voids within the steel. Thus a gas pressure is set up in the voids and this may be sufficient to cause blisters to appear either during pickling or during subsequent processing such as hot-dip galvanising.

The embrittlement effect can be largely removed by ageing the steel at about 150°C, but even then the original ductility is not entirely restored.

In the estimation of the degree of embrittlement, the temperature and rate of testing have an important effect. Thus the embrittlement tends to disappear at very low and very high temperatures, and it is reduced at high strain rates.

Several theories of the mechanism of embrittlement have been put forward³⁻⁵ and further details are given in Section 8.4.

Acids Used for Pickling

Before steel strip or rod can be cold rolled, tinned, galvanised, or enamelled, etc. any scale formed on it by previous heat treatment must be removed. This can be done by mechanical and other special methods, but if a perfectly clean surface is to be produced, acid pickling is preferred, either alone or in conjunction with other pretreatment processes.

Sulphuric Acid

Sulphuric acid is used to a very large extent for pickling low-alloy steels. The rate at which it removes the scale depends on (a) the porosity and number of cracks in the scale, (b) the relative amounts of wüstite, decomposed wüstite, magnetite and haematite in the scale, and (c) factors affecting the activity of the pickle.

Temperature is the most important of the factors affecting pickle activity. In general, an increase of 10°C causes an increase in pickling speed of about 70%. Agitation of the pickle increases the speed since it assists the removal of the insoluble scale and rapidly renews the acid at the scale surface. Increase in acid concentration up to about 40% w/w in ferrous sulphate-free solutions, and up to lower concentrations in solutions containing ferrous sulphate, increases the activity. Increase in the ferrous sulphate content at low acid concentrations reduces the activity, but at 90–95°C and at acid concentrations of about 30% w/w it has no effect.

For economic reasons, continuous wide mild steel strip must be pickled within 0·5–1·0 min. To achieve this, the strip is flexed to increase the number of cracks in the scale and then passed through four or five long tanks. Acid of 25% w/w strength enters the last tank and flows countercurrent to the strip, and finally emerges from the first tank as waste pickle liquor containing about 5% w/w acid and almost saturated with ferrous sulphate. To increase the activity of the pickle to a maximum, live steam is injected to agitate the pickle and to raise the temperature to about 95°C. The scale on the edges of the strip and on the leading and trailing ends is usually more difficult to pickle than that in the centre. Consequently, whereas the centre scale is removed in the first or second tank, the remainder is removed only in the last tank. After pickling, the strip is thoroughly rinsed and dried.

For the batch pickling of rod, sheet, tube or strip in coil form, short pickling times are not so important, and pickling times of several minutes at 60–80°C in 5–10% w/w acid are common. The acidity is maintained by the addition of fresh strong acid, until the pickle is nearly saturated with ferrous sulphate, and then the acidity is worked down to 1 or 2%.

Electrolytic pickling

Anodic pickling Sulphuric acid is also used in electrolytic pickling. Anodic pickling, which is suitable only for lightly scaled steel, has the advantage that no hydrogen embrittlement is produced, but the base metal is attacked as the scale is being removed. Under 'active' conditions the steel is rapidly attacked, and the surface is left rough and covered with smut. Under 'passive' conditions the attack on the steel is reduced, and the evolved oxygen mechanically

removes the smut and other surface contaminants, leaving the steel with a clean satin finish which provides good adhesion for electrodeposits.

Cathodic pickling Cathodic pickling protects the base metal from acid attack while the scale is being reduced to spongy iron, but there is a danger of hydrogen embrittlement, and particularly if the acid contains arsenic. In the Bullard-Dunn⁶ process the steel is made cathodic at 0.065 A/cm^2 in hot 10% w/w acid containing a trace of tin or lead. The tin or lead plates out on the descaled areas as a very thin coating, and owing to the high hydrogen overvoltage of these metals the formation of hydrogen ceases and so the current is diverted to the remaining scaled areas. The tin or lead can be removed by means of anodic alkali treatment, or may be left on and used as a base for subsequent painting.

A.c. pickling Alternating current pickling can be used where it is difficult to feed current into the steel by direct electrical connection, e.g. in the case of strip moving at high speed. In this process the electrodes are placed above and below the strip and so while one face of the strip is anodic the other is cathodic, the polarity being reversed during each cycle of alternation. The application of $0.11\text{--}0.16 \text{ A/cm}^2$ to strip in 10% v/v H_2SO_4 at 88°C has been claimed to increase the pickling speed by 35%⁷. Alternatively, cathodic/anodic pickling may be employed on moving strip without the use of contacts. The moving strip is made cathodic with anodes in one tank and anodic with cathodes in the following tank, the strip itself carrying the current from tank to tank.

Hydrochloric Acid

Although hydrochloric acid is more expensive than sulphuric acid, it is gradually replacing the latter for pickling mild-steel strip, because the waste liquor can be recovered more economically. It is more active than sulphuric acid at an equivalent concentration and temperature, probably because the rates of diffusion of acid to, and ferrous ions from, the steel surface are greater. Consequently it is used cold for pickling in open tanks and for highspeed pickling of mild steel strip it is used hot in covered tanks to prevent loss of acid by volatilisation. It is more suitable than sulphuric acid for pickling articles which have to be tinned or galvanised since it gives less smut on the steel. In addition, any residual iron chloride left on the steel can be rinsed off more readily than residual iron sulphate deposits. Hydrochloric acid, however, readily dissolves the detached magnetite and haematite and, consequently, the ferric ion produced increases the rate of attack on the steel and thus increases the acid consumption.

Phosphoric Acid

Although phosphoric acid can be used for pickling steel, it is seldom used simply for scale removal since it is so expensive and slow in action. Steel plates are often initially descaled in sulphuric acid and then, after rinsing, immersed in 2% phosphoric acid containing 0.3–0.5% iron at 85°C for 3–5 min⁸. The plates are then allowed to drain and dry without further

rinsing. This treatment produces a grey film of iron phosphates on the steel surface, which provides a good base for subsequent painting.

Nitric Acid

Nitric acid does not dissolve scale so readily as mineral acid. A cold 5% w/v nitric acid solution is used to etch bright mild-steel strip when the smut resulting from the acid attack is easily and completely removed with a light brushing. It is also used in conjunction with sulphuric acid for cleaning bright annealed strip, which is difficult to pickle in mineral acid. This difficulty arises when certain types of rolling lubricant have not been thoroughly removed before annealing. During annealing, these lubricants polymerise to gum-like materials which are unattacked by mineral acid but are oxidised and removed with nitric acid. For this type of steel, pickling in a bath containing 20% w/v H_2SO_4 and 4% w/v HNO_3 , with a trace of HCl , at 30°C for 4–6 min has been recommended⁹.

Pickling of Alloy Steels

The furnace scales which form on alloy steels are thin, adherent, complex in composition, and more difficult to remove than scale from non-alloy steels. Several mixed acid pickles have been recommended for stainless steel, the type of pickle depending on the composition and thickness of the scale¹⁰. For lightly-scaled stainless steel, a nitric/hydrofluoric acid mixture is suitable, the ratio of the acids being varied to suit the type of scale. An increase in the ratio of hydrofluoric acid to nitric acid increases the whitening effect, but also increases the metal loss. Strict chemical control of this mixture is necessary, since it tends to pit the steel when the acid is nearing exhaustion. For heavy scale, two separate pickles are often used. The first conditions the scale and the second removes it. For example, a sulphuric/hydrochloric mixture is recommended as a scale conditioner on heavily scaled chromium steels, and a nitric/hydrochloric mixture for scale removal. A ferric sulphate/hydrofluoric acid mixture has advantages over a nitric/hydrofluoric acid mixture in that the loss of metal is reduced and the pickling time is shorter, but strict chemical control of the bath is necessary.

Electrolytic pickling of stainless steel in 5–10% w/v sulphuric acid at 50°C can be used for removing the majority of the scale. The strip is first made anodic, when a little metal dissolves, and then cathodic, when the evolved hydrogen removes the loosened scale. To complete the pickling, a nitric plus hydrofluoric acid dip is given for austenitic steels and a nitric acid dip for ferritic steels. Austenitic and ferritic stainless steels are not subject to hydrogen embrittlement with reducing acids, but steels of relatively high carbon content in the hardened state may be.

Organic Inhibitors

During the pickling of scaled steel the thinner and more soluble scale is removed before the thicker and less soluble scale. Consequently, some

exposed base metal is attacked before the pickling operation is complete. In order to reduce this acid attack to a minimum, organic inhibitors are used. Their use also leads to less acid being consumed and less smut and carbonaceous matter is left on the steel. Because of the reduced hydrogen evolution, the amount of acid spray and steam consumption are also reduced.

Although a good inhibitor reduces the acid attack, it does not prevent the attack of oxidising agents on the exposed base metal. Thus the ferric ions resulting from the gradual dissolution of the detached magnetite and haematite attack the exposed steel even in the presence of an inhibitor, and are reduced to ferrous ions.

The inhibitor should not decompose during the life of the pickle nor decrease the rate of scale removal appreciably. Some highly efficient inhibitors, however, do reduce pickling speed a little. It would be expected that since the hydrogen evolution is reduced the amount of hydrogen absorption and embrittlement would also be reduced. This is not always the case; thiocyanate inhibitors, for example, actually increase the absorption of hydrogen.

Since inhibitors form insulating films on the steel, they interfere with any subsequent electroplating. In many cases, however, the films can be removed prior to plating by anodic cleaning or by a nitric acid dip.

Surface-active agents are often added to the pickle if the inhibitor has no surface-active properties. They assist the penetration of the acid into the scale, reduce drag-out losses, and form a foam blanket on the pickle. This blanket reduces heat losses and cuts down the acid spray caused by the hydrogen evolution.

Many organic substances soluble in acid or colloiddally dispersible have been shown to have inhibiting properties. The most effective types contain a non-polar group such as a hydrocarbon chain and a polar group such as an amine. They contain oxygen, nitrogen, sulphur, or other elements of the fifth and sixth groups of the Periodic Table. They include alcohols, aldehydes, ketones, amines, proteins, amino acids, heterocyclic nitrogen compounds, mercaptans, sulphoxides, sulphides, substituted ureas, thio-ureas and thioazoles.

The efficiency of an inhibitor under a given set of conditions is expressed by the formula

$$I = \frac{A - B}{A} \times 100$$

where I is the per cent inhibition efficiency. A the corrosion rate in uninhibited acid, and B the corrosion rate in acid containing a certain concentration of inhibitor.

In general the efficiency increases with an increase in inhibitor concentration—a typical good inhibitor gives 95% inhibition at a concentration of 0.008% and 90% at 0.004%. Provided the inhibitor is stable, increase in temperature usually increases the efficiency although the actual acid attack may be greater. A change in acid concentration, or in type of steel, may also alter the efficiency. Thus, the conditions of a laboratory determination of efficiency should closely simulate the conditions expected in commercial practice.

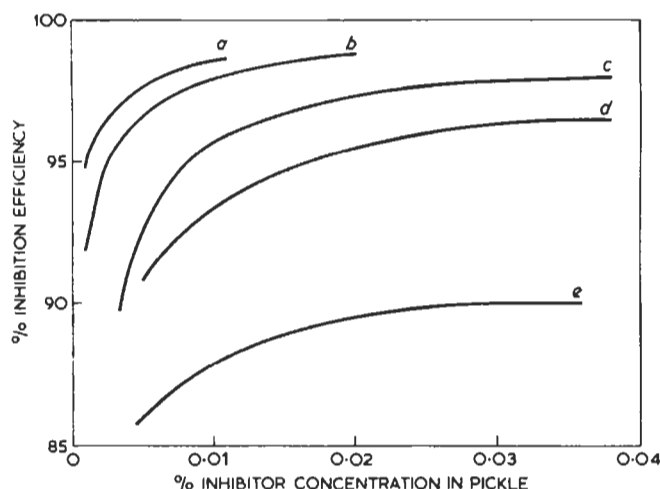


Fig. 11.4 Relationship between % inhibitor efficiency and inhibitor concentration in 6% w/w H_2SO_4 . Curve (a) di-*o*-tolyl thiourea; (b) mono-*o*-tolyl thiourea; (c) commercial inhibitor containing 20% di-*o*-tolyl thiourea; (d) commercial inhibitor containing 20% di-phenyl thiourea; (e) gelatin

Table 11.3 Pickling solutions for non-ferrous metals

<i>Metal</i>	<i>Acid</i>	<i>Temperature</i>	<i>Time</i>
Copper and brass (60–90% Cu, 10–40% Zn)	7–25% w/w H_2SO_4 or 15–25% w/w HCl	15–60°C 15°C	1–10 min 1–3 min
Aluminium bronze (82–95% Cu, 5–10% Al, 0–5% Fe, 0–5% Ni)	Scale conditioned with 10% w/w NaOH followed by H_2SO_4 or HCl as above	75°C	2–5 min
Copper-silicon alloys (96–97% Cu, 1–3% Si)	7–25% w/w H_2SO_4 + 1–3% w/w HF	15°C	1–5 min
Nickel-copper alloys (55–90% Cu, 10–30% Ni, 0–27% Zn)	10% w/w HCl + 1.5% w/w CuCl_2	80°C	30 min
Nickel-chromium alloys (35–80% Ni, 16–20% Cr, 0–45% Fe, 0–2% Si)	Scale conditioned with 20% NaOH + 5% w/w KMnO_4 followed by 20% w/w HNO_3 + 4% w/w HF	100°C 50°C	1–2 h 5–30 min
Aluminium alloys (0–10% Cu, 0–10% Mg, 0–6% Zn, 0–12% Si)	25% w/w H_2SO_4 + 5% w/w CrO_3 40% w/w HNO_3 + 1.5% w/w HF	65°C 15°C	20 min 1–5 min
Magnesium alloys (0–10% Al, 0–3% Zn, 0–0.2% Mn)	10–20% w/w CrO_3 + 3% w/w H_2SO_4	100°C 25°C	1–30 min 15 s

Figure 11.4 shows the relationship between efficiency and concentration of some thiourea derivatives and gelatin in the pickling of cold-reduced and annealed strip in 6% w/w sulphuric acid at 85°C. The thiourea derivatives, diluted with sodium chloride, gelatin and a wetting agent, are used commercially. Mono- and di-*o*-tolyl thioureas are stable in this pickle for at least 50 h, but diphenyl thiourea and gelatin decompose after four or five hours.

Inorganic Inhibitors

Inorganic inhibitors are salts of metals having a high hydrogen overvoltage, e.g. antimony and arsenic. The inhibiting action is associated with the formation of a coating of the metal, which, being cathodic to the steel and having a high hydrogen overvoltage, prevents the discharge of hydrogen ions and so stops the dissolution of the steel. These inhibitors are seldom used in commercial practice, but antimony chloride dissolved in concentrated hydrochloric acid is used in the laboratory for stripping deposits of zinc, cadmium, tin and chromium from steel, and with the addition of stannous chloride for removing scale and rust¹¹.

Further details of inhibitors for acid solution are given in Section 17.2.

Acid Pickling of Non-ferrous Metals

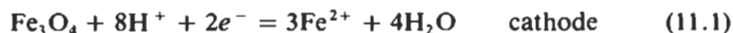
Table 11.3 summarises the pickling conditions for removing oxide and scale from some of the more important non-ferrous metals and alloys.

Recent Developments

Mechanisms of Scale Removal from Steel with Acid

The mechanisms of oxide dissolution and scale removal have been widely studied in recent years. This work has been thoroughly reviewed by Frenier and Growcock¹², who concluded, in agreement with others¹³, that oxide removal from the surface of steel occurs predominantly by a process of reductive dissolution, rather than by chemical dissolution, which is slow in mineral acids.

In this process the reduction of the ferric components of the scale is coupled to oxidation of the base metal, both reactions yielding ferrous species readily soluble in the acid. For magnetite the processes are as shown in equations 11.1 and 11.2.



Scale removal is also assisted by the dissolution of the underlying metal by normal acid corrosion processes, which undermines the scale, and by the physical effect of hydrogen gas evolved in this latter reaction. Some authors¹⁴ attribute major effects to the latter.

In general there does not appear to be any direct correlation between the rate of the chemical dissolution of oxides and the rate of scale removal, although most work on oxide dissolution has concentrated on magnetite. For example, Gorichev and co-workers have studied the kinetics and mechanisms of dissolution of magnetite in acids^{15,16} and found that it is faster in phosphoric acid than in hydrochloric, whereas scale removal is slower. Also, ferrous ions accelerate the dissolution of magnetite in sulphuric, phosphoric and hydrochloric acid¹⁶, whereas the scale removal rate is reduced by the addition of ferrous ions. These observations appear to emphasise the importance of reductive dissolution and undermining in scale removal, as opposed to direct chemical dissolution.

As further confirmation of this Rozenfeld¹³ has reviewed Russian work on this subject and reports that in pickling with sulphuric acid the amount of acid used in scale dissolution is only about one-tenth that consumed by the dissolution (corrosion) of the underlying metal. However, in hydrochloric acid the direct scale dissolution occurs to a much greater degree, and is responsible for about 40% of the acid consumption.

A mechanism such as that given above provides explanations for the known effects of many process variables¹⁴. The reductive dissolution and undermining processes require access of the acid to the metal surface, hence the benefits obtained by the deliberate introduction of cracks in the oxide by cold-working prior to pickling. Also the increase in pickling rate with agitation or strip velocity can be explained in terms of the avoidance of acid depletion at the oxide-solution interface.

Acids Used for Pickling

Currently the importance of hydrochloric acid is increasing, with sulphuric acid still widely used, and with some applications for other mineral acids.

Pickling of Alloy Steels

The chromium-containing oxides on stainless steels are more resistant to reductive dissolution and harder to remove than oxides on mild steel. Typically mixed acids and multistage treatments are used and many formulations have been reported¹⁷. Scale conditioning can be carried out in acids, in molten salts (e.g. sodium hydroxide plus sodium nitrate) or in alkaline solutions (e.g. alkaline permanganate). Scale removal can be obtained with a variety of acids, the commonest being a nitric/hydrofluoric mixture. Rozenfeld¹³ also reports effective pickling with ferric sulphate plus sulphuric acid mixtures and considers that the effect of the ferric ions is to speed up the dissolution of the underlying metal. Organic acids, such as citric acid, also have a role in the cleaning of lightly corroded alloy steels¹⁸.

Organic Inhibitors

The principles behind the selection of effective inhibitors for steel in the various acids have been reviewed by Schmitt¹⁹ and Gardner²⁰. The selection

of an inhibitor is dependent on both the metal and the acid. For steel, in general, nitrogen-based inhibitors (e.g. amines and heterocyclic compounds) are used in hydrochloric acid, whereas sulphur-containing ones (e.g. thiourea and its derivatives) find more favour in sulphuric acid.

Given the reductive dissolution process involved and the contributions from undermining and hydrogen evolution in scale removal, inhibitors might be expected to affect the rate of this removal. Also, if the inhibitor adsorbs on the oxide surface then the rate of chemical dissolution of the oxide may be affected. Experimental evidence suggests that these effects may occur, depending on the acid and the inhibitor. Cumper²¹ has shown that pyrrole and indole can increase the rate of dissolution of magnetite in hydrochloric acid. It has been reported²² that commercial amine-based inhibitors can either increase or decrease the rate of scale removal in the same acid. Other reports suggest that the presence of inhibitor has little effect on scale removal rate in hydrochloric acid but markedly decreases it in sulphuric acid. One area that has not been widely studied is the effectiveness of inhibitors on scaled surfaces, but there is experimental evidence that the presence of magnetite scales can significantly affect the performance of nitrogen-based inhibitors in alkaline solutions used for chemical cleaning.

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11.3 Chemical and Electrolytic Polishing

Introduction

The choice of polishing method for the finishing of metal components depends not only on the type of finish required but also on the state of the metal surface at that stage of the production route. The bulk of surface soil – both physically and chemically attached – will have been removed in primary cleaning and pickling stages, and so polishing is concerned with removal of last traces of soil, but more particularly the removal of surface roughness, blemishes and burning arising as the result of prior fabrication processing. Mechanical polishing and buffing can be a very effective method, but has the disadvantage that it work-hardens the surface, thereby inducing a degree of residual compressive stress, and may also promote the incorporation of soil, oxide, polishing compound etc. into a soft surface and which may consequently become contaminated to a significant depth. Nevertheless, for small components mass finishing in polishing barrels has become an acceptable alternative production method.

In contrast chemical and electrolytic polishing enables a smooth level surface to be produced without any residual stress being developed in the surface because the surface is removed by dissolution at relatively low chemical potential and at relatively low rates in such a way that metallic surface asperities are preferentially removed. For this to be most effective the solution properties must be optimised and the pretreatment must leave an essentially bare metal surface for attack by the electrolyte.

A variety of synonyms have been used for these processes but they can quickly be placed in two categories.

1. Chemical polishing which relies entirely on a solution without any externally applied current. Other processes have been termed 'bright dipping', and these are very similar but usually produce lustre without good levelling and the high level of specular reflectivity implied by the term polishing.
2. Electropolishing which exploits a generally similar type of solution, but introduces anodic currents as an additional means of dissolution thereby providing better control of rapid processing. 'Electrosmoothing' and 'electrobrightening' are terms used to describe inferior finishes which may have lustre but have lower specular reflectivity.

Either process can only be successful if good quality metal is supplied, for example with uniform grain size and freedom from non-metallic inclusions, and the pretreatments are applied conscientiously.

The choice between chemical and electrolytic polishing is often governed by the quality of finish and that obtainable from existing processes. But those being equal, it is generally true to say that initial and operating costs are less for chemical polishing because of the electrical requirements for electropolishing, but that capital costs can be greater in view of the greater corrosivity of the solutions themselves and the fact that in use they produce considerable problems with corrosive acid fumes.

The characteristics of a polished surface are that it should be level on a macroscopic scale related, for example, to machine and grinding marks of 1–5 μm depth, and be smooth and bright on a microscopic scale typically 1–100 nm size for fine grained metal. To achieve dual levelling and smoothing a solution must satisfy three requirements by including three types of constituent:

1. an oxidising agent capable of dissolving metal in solution through a surface film which smooths any preferential dissolution on an atomic level;
2. a contaminating agent which controls the thickness of that oxidant film—if it is too thick the metal passivates and polishes extremely slowly, if it is too thin or absent preferential etching can occur;
3. a diffusion layer promoter which provides a viscous liquid adjacent to the surface and which promotes macroscopic levelling.

The common defects arising in processing include etching—preferential attack of grain boundaries—which occurs if the film has not fully formed; it may be exploited in certain circumstances because the finish can be artistically attractive and the surface area may be increased. Pitting occurs if the film is disrupted at local sites, either by incorrect balance of film former/contaminant or by gas evolution on the surface.

Although most solutions satisfy the three-component criterion they have usually been established by empirical methods and their compositions can be found by referring to tables on a 'recipe-book' basis^{1–3}. Many have been extensively explored by metallographers in search of improved preparation techniques, notably for electron microscopy^{4–6}.

Industrial application of these processes whilst being widespread only involves large proportions of metal being processed in a few specialised instances, for example anodised aluminium for reflectors. Industrial use is justified by virtue of improved reflectivity and brightness, appearance and occasionally corrosion resistance. It is normally an expensive pretreatment for anodising and electroplating unless the high level of reflectivity is essential, but it does provide a most effective means of removing excessive mechanical burring and roughness, highly stressed surface layers of metals sensitive to stress-cracking failure and thin alloyed layers arising incidentally from prior processing. In some of these respects it may be considered a sister process to electrochemical machining.

Bright Dipping and Chemical Polishing

As already indicated, bright dipping is essentially a simpler and cheaper process than chemical polishing carried out by simple immersion in a strong, often hot, acid solution for a time of 0.5–5 min. Proprietary forms of these solutions may have inhibitive additives to reduce pitting and gas-evolving tendencies. The rate of metal attack is high, substantial acid fume arises and the reduction of rate of attack as the solution becomes depleted may be combatted to some extent by increasing the temperature. The surface should be rinsed quickly after removal from the bright-dip solution, otherwise 'transfer etch' will occur; this is essentially attack by the residual acid film and may be accelerated by atmospheric oxygen absorbed by the film during transfer. A typical bright-dip solution for copper might be an aqueous solution containing 40% H_2SO_4 and 10% HNO_3 . In this solution nitric acid is the oxidant (A) and sulphuric acid the contaminant (B); there is no diffusion layer promoter. It is used cold and gives a good bright surface in 0.5–2 min accompanied by substantial fuming. Improved performance can be achieved by adding 5–15 g/l hydrochloric acid, and increasing the nitric acid content to 20%. Solutions of this type are widely used in industry⁷.

Chemical polishing, yielding a surface of high specular reflectivity, exploits fully optimised bright dip solutions often achieved by the further addition of phosphoric acid at the expense of the residual water. Because phosphoric acid is relatively viscous at lower temperatures (e.g. less than 40°C) it can act as diffusion layer promoter (C), but its presence increases the chemical costs considerably.

By invoking these principles such solutions may now be designed for most metals, and in the case of atmospheric metals a range of alkaline solutions may also be considered. For the more reactive metals such solutions become increasingly strong, hazardous and expensive. A typical, solution for the chemical polishing of titanium could contain 40% v/v HNO_3 , 30% v/v H_2SO_4 and 30% v/v of 40% HF. The titanium would be exposed to this solution for 30s at 70–80°C. A list of recommended solutions for the commoner metals is given in Table 11.4; for other metals reference should be made elsewhere^{1–6}.

A notable recent achievement has been the development of a first class chemical polishing solution for aluminium. The older solutions are essentially bright dips, requiring a 'desmutting' post-treatment which may arise either from intermetallic compounds within the aluminium alloy or from excessive loose oxide on the surface, based on nitric-sulphuric-phosphoric acid mixtures⁸. However, the addition of small amounts of a noble metal to the solution improves the degree of brightening obtained substantially and the resulting process has proportional features as Phosbrite (trade mark of Albright and Wilson plc). One of the best compositions is 77.5% v/v H_3PO_4 , 16.5% v/v H_2SO_4 , 6.0% v/v HNO_3 , and 0.5–2.0 g/l CuSO_4 . Copper is deposited on the surface of the aluminium as a fine colloidal precipitate and may be washed or wiped off leaving a highly specular surface. The mechanism of its behaviour has been the subject of many investigations^{9–12}, and the process may be regarded as highly successful such that its use for the industrial production of reflectors and mirrors is now widespread, replacing electroplating.

Table 11.4 Chemical polishing solutions

<i>Metal</i>	<i>Solution</i>	<i>Conditions</i>
Aluminium	1. Phosphoric acid	80% v/v
	Nitric acid	5 v/v
	Acetic acid	5
	Water	10 v/v
	2. Phosphoric acid	75% w/w
	Hydrogen peroxide	3.5 w/w
	Water	rem w/w
	3. Phosphoric acid	70% v/v
	Sulphuric acid	20 v/v
Cadmium	Nitric acid	10 v/v
	Copper nitrate	5 g/l
	1. Chromium trioxide	85 g/l
	Sulphuric acid	1–2 g/l
	2. Sulphuric acid	0.3% v/v
	Hydrogen peroxide (30 vol)	7 v/v
Copper	1. Sulphuric acid	45% v/v
	Nitric acid	22 v/v
	Hydrochloric acid	1–2 v/v
	Water	33 v/v
Mild and Carbon steels	1. Oxalic acid	25 g/
	Hydrogen peroxide (100 vol)	13 g/l
	Sulphuric acid	0.1 g/l
	2. Nitric acid	40% v/v
	Hydrofluoric acid (40%)	10 v/v
	Water	50
	3. Hydrogen peroxide (30 Vol)	80% v/v
	Hydrofluoric acid (40%)	5 v/v
	Water	15 v/v
Nickel	Glacial acetic acid	50% v/v
	Nitric acid	30 v/v
	Phosphoric acid	10 v/v
	Sulphuric acid	10 v/v
Titanium	1. Nitric acid	40% v/v
	Sulphuric acid	30 v/v
	Hydrofluoric acid (40%)	30 v/v
Zinc		
	1. Chromium trioxide	220 g/l
	Sodium sulphate	12–30 g/l
	(followed by dip in 5 g/l sulphuric acid for 1–10 s)	

All acids used are the most concentrated forms available. Solutions should be made up by using water or the acid solution containing most acid as the base to which other acids are added. All solutions should be mixed with care using cooling and continuous mixing.

Electropolishing

Electropolishing techniques utilise anodic potentials and currents to aid dissolution and passivation and thus to promote the polishing process in solutions akin to those used in chemical polishing. The solutions have the same basic constitution with three mechanistic requirements—oxidant (*A*), contaminater (*B*) and diffusion layer promoter (*C*)—but, by using anodic currents, less concentrated acid solutions can be used and an additional variable for process flexibility and control is available.

The electrochemical characteristics of electropolishing can be seen by referring to a typical polarisation (potential versus current density) diagram (Fig. 11.5). The aim is to provide a 'polishing plateau' at constant current over a substantial range of potential, but the value of that constant current can be fairly critical. Thus in (a) the metal is passivated and in (c) it dissolves under solution diffusion control, neither condition giving effective electropolishing. A wide potential range is desirable in order to provide process flexibility, but does indicate the need to use potential control as a means of controlling the process (Fig. 11.6). Potentiometric control, or potentiostatic if exercised by a potentiostat instrument, is clearly preferred, but demands the use of a good reference electrode to be effective. The series, or galvanostatic, technique is most generally used in industry because of its convenience in using conventional transformer/rectifier equipment, but can only be considered equivalent in the fortuitous circumstance of Fig. 11.5b where the current 'fall back' is slight. The all-too-common habit of quoting a cell voltage for electropolishing conditions is consequently rather meaningless, dependent as it is on electrolyte conductivity and inter-electrode spacing in the process cell used.

Referring to Fig. 11.5b, the initial rise in current corresponds to simple metal dissolution, expressed quantitatively through the Tafel equation relating potential and current logarithmically, and for multi-grained metals

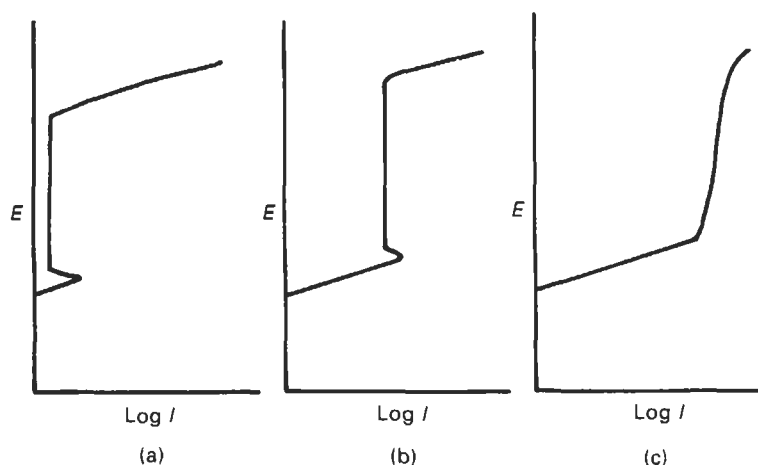


Fig. 11.5 Anodic polarisation (potential-current density) curves for nickel in (a) dilute sulphuric acid, (b) cold 10 M sulphuric acid, and (c) hot or agitated 10 M sulphuric acid

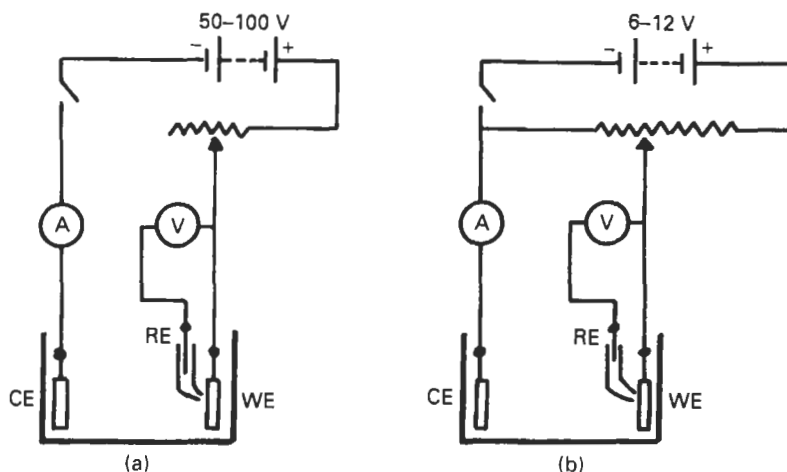


Fig. 11.6 Simple electrical circuitry for electropolishing

can be used to electro-etch the surface (see 'Electrolytic Etching' below). At a certain critical potential film formation can occur and dissolution is limited by that critical metal/electrolyte interface whose stability depends both on metal film forming tendencies and solution viscosity: if the film is too stable, the current is very low and any polishing takes days or weeks to be accomplished. If mass transfer in the viscous layer is increased by agitation or increased temperature the requisite levelling action may be lost. At higher anodic potentials the current rises sharply and, while polishing may still occur, it is accompanied by pitting and is therefore an unacceptable condition. Such behaviour is usually associated with oxygen evolution becoming thermodynamically possible (the overpotential being over 1 V corresponding to a reaction potential of at least +1.5 V (SHE)). The oxygen bubbles evolve at discrete favoured sites causing local film breakdown and stirring which increases local dissolution rates resulting in pit formation. A flexible process has a polishing plateau over a range of ~ 1 V, and ~ 0.3 V is a minimal requirement.

The simplest and most thoroughly studied solutions are those based on phosphoric acid at low temperatures ($<35^{\circ}\text{C}$) which alone can fulfil all three requirements of acid solvent, film former (as metal phosphate) and diffusion agent by virtue of its viscosity. Thus copper and its main alloys of brasses and bronzes can be very effectively electropolished in 60–70% orthophosphoric acid with the temperature maintained below 35°C ; under other conditions copper passivates or dissolves freely under mass transfer controlled conditions, but by varying the conditions appropriately polishing can be continued under mild agitation. An annotated polarisation curve is given in Fig. 11.7; readers are referred to recent studies for more detailed aspects^{13–17}.

Only copper can be electropolished in such a simple solution, but by minor modification other metals can be treated. Such modifications include (a) increasing the acidity, or (b) increasing the oxidant level for aluminium, iron and steel, nickel alloys etc:

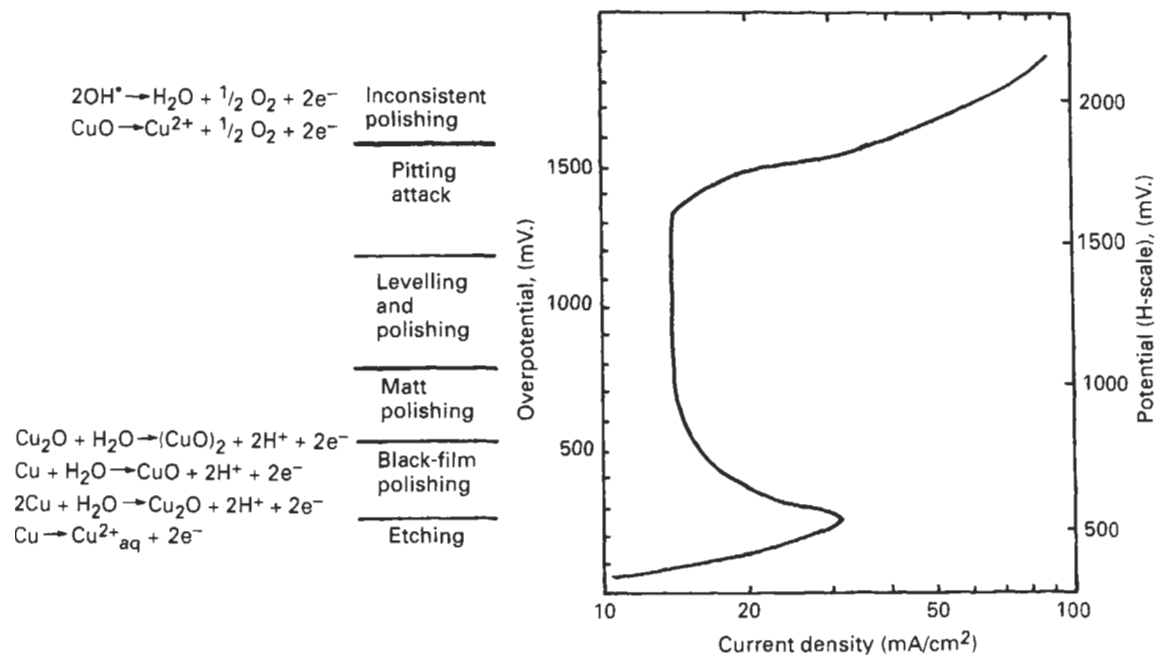


Fig. 11.7 Annotated anodic polarisation curve for the electropolishing of copper in orthophosphoric acid at 18°C

- (a) 500 ml/l H_3PO_4 , 450 ml/l H_2SO_4 , balance water; 20–30 A/dm² at 60–90°C.
 (b) 600 ml/l H_3PO_4 , 150 g/l CrO_3 , balance water; 1–10 A/dm² at 35–75°C.

The solutions cease to electropolish well once they contain substantial amounts of metal or when the potential is incorrectly set; the departure from good finishing is recognised by the development of etch or pit features, often at edges or recesses, and this led Hoar *et al.*^{18,19} to express the critical parameters in diagrammatic form (Fig. 11.8) where the line x-x represents the ideal condition of anodic electropolishing.

Electropolishing is thus a condition characteristic of both the solution and the metal involved; nevertheless, several attempts have been made to develop a 'universal' electropolishing solution. For some years the Jacquet Solution^{1,20} was believed to offer this opportunity because it was so successful for mild and alloy steels. This is an aqueous solution typically containing 15.7 vol% perchloric acid (70%, $d = 1.6$) and 76.5 vol% acetic anhydride, and used at a temperature of 17–22°C. However, the various serious hazards associated with this solution, both during initial mixing and long-term use, have militated against its use. The hazards have been discussed by both Jacquet¹ and Tegart² and involve the highly oxidising nature of perchloric acid, the large heat of hydration of acetic anhydride, the large heat of mixing (perchloric acid always contains at least 30% excess water) and the high electrical resistivity giving rise to heating during use. Several well-known accidents have occurred and its use is not recommended²¹ because a modified solution 5–20% perchloric acid in methanol has proved to be safer

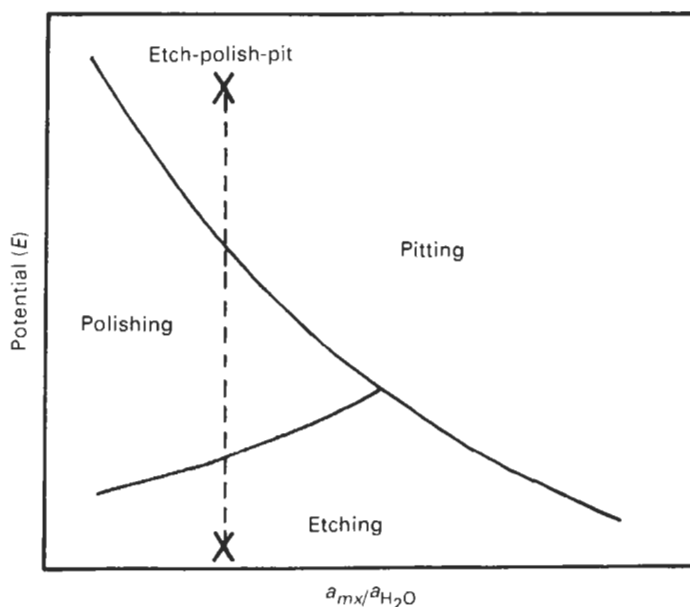


Fig. 11.8 'Hoar' diagram illustrating domains of anodic behaviour

(but care is still needed!) and virtually universal in behaviour^{22,23}. Perchloric acid is the strongest oxidant acid known, and therefore dissolves most metals, while methanol acts as a viscous agent at low temperatures. For some metals, the temperature may need to be as low as -50°C but -10 to $+10^{\circ}\text{C}$ is most usual. It has been studied as a 'universal' electropolishing solution²³ and has been proven for metals such as aluminium^{22,24}, titanium^{25,26} and all steels²⁷. It is never used for metals, such as copper, for which a good, simple alternative exists.

A very substantial literature may now be found for electropolishing solution formulation and Table 11.5 gives some of the well-established compositions and operating conditions. Further solutions may be found in the standard reference books^{1,2,8,28,29}, and for specialist applications and metals a literature search should yield useful suggestions. More recently published works include an excellent review of the theory of electropolishing⁵⁷ and two papers relating to mass transport effects during electropolishing^{58,59}.

Table 11.5 Electropolishing solutions for the commoner metals

<i>Metal</i>	<i>Solution</i>	<i>Conditions</i>
Aluminium	Electropolishing	
	1. Ethanol	80% v/v
	Perchloric acid	20 v/v
		Temp. $< 20^{\circ}\text{C}$ Time 15–120 s Voltage 20–70 V
	2. Glacial acetic acid	70% v/v
	Perchloric acid	30 v/v
		Temp. $< 20^{\circ}\text{C}$ Time 5–15 min Voltage 20–70 V
	3. Ethanol	40% v/v
	Phosphoric acid	40 v/v
	Water	20 v/v
Cadmium	Electrobrightening*	
	4. Fluoboric acid	2.5% w/w
		Temp. 29°C Time 5–10 min Voltage 15–30 V Current density 1–2 A/dm ²
	5. Sodium carbonate	15% w/w
	Sodium phosphate	5% w/w
		Temp. 80°C Time 20 s Voltage 10–20 V 2–3 A/dm ²
	6. Sulphuric acid	4–45% w/w
	Phosphoric acid	40–80 w/w
	Chromium trioxide	0.2–9 w/w
	*Desmut in either	
Copper	Sulphuric acid	10% v/v
	or	
	Phosphoric acid	1–4% w/w
	Chromium trioxide	0.5–2% w/w
		25°C for 15–30 s 90°C for 30 s
	1. Phosphoric acid	40% v/v
	Water	60 v/v
		Temp. $< 30^{\circ}\text{C}$ Time 5–15 min Voltage 1–2 V
	1. Phosphoric acid	66% v/v
	Water	34 v/v
Gold		Temp. $< 35^{\circ}\text{C}$ Time 10–4 min Voltage 1–2V
	1. Potassium cyanide	80 g/l
	Potassium carbonate	40 g/l
	Gold chloride	50 g/l
		Temp. $15\text{--}30^{\circ}\text{C}$ Time 2–4 min Voltage 4–8 V

Table 11.5 (continued)

<i>Metal</i>	<i>Solution</i>		<i>Conditions</i>
Iron, carbon steels	1. Glacial acetic acid Perchloric acid	80–90% v/v	Temp. <25°C
		20–11% v/v	Time 1–10 min Voltage 10–70 V
	2. Methanol or ethanol Perchloric acid Glycerol	80–90% v/v	Temp. <20°C
		20–10 v/v	Time 1–10 min
		5–20% v/v	Voltage 10–70 V
High alloy stainless steels	1. Sulphuric acid Water	75% v/v	Temp. 15–35°C
		25 v/v	Time 1–10 min Voltage 5–20 V
	2. Methanol/perchloric (as for iron)		
	3. Chromium trioxide Phosphoric acid Sulphuric acid Water	70–120 g	Temp. 35–50°C
		450–650 ml	Time 10–60 min
		400–120 ml 150–250 ml	Voltage 1–3 V
Magnesium	1. As for aluminium (nos. 1, 3)		
Nickel	1. Sulphuric acid	70% v/v	Temp. 20°C Time 1–5 min Current density 2–3 A/dm ²
Silver	1. As for gold		
Tin	1. Methanol/perchloric (as for iron)		
	2. Ethanol/perchloric (as for aluminium)		
	3. Phosphoric acid Sulphuric acid Water	40–60% v/v 15–9% v/v 45–31% v/v	Temp. 15–30°C Time 5–15 min Voltage 1–3 V
Zinc	2. Methanol/perchloric (as for iron)		
	2. Ethanol/perchloric (as for aluminium)		
	3. Methanol Nitric acid (do not use ethanol)	65% v/v 35% v/v	Temp. 15–30°C Time 10–60 s Voltage 40–70 V

All acids used are the most concentrated forms available. Solutions should be made up by using water or the acid solution containing most acid as the base to which other acids are added. All solutions should be mixed with care using cooling and continuous mixing.

Electrolytic Etching

It has already been pointed out that the initial stage of polarisation during electropolishing is one of dissolution, which is often termed etching in view of the tendency to produce faceted surfaces owing to differential dissolution across the surface. It is clear that non-electrolytic etching can also occur if the chemical solution is able to differentiate between different sites and types of site on the surface, notably grains and grain boundaries where small

differences of composition and surface energy are in effect exploited. Oxidants are particularly adept to such discrimination, thus giving rise to a well-established tradition of metallographic etching reagents—ferric chloride or ammonium persulphate for copper, nital for mild steel etc. While metallographic etching remains a major use for this technique, industrial uses have been developed for a variety of purposes including aesthetic appearances for art and craft work, specialised surface cleaning and increase of true surface areas for reactor surfaces of, for example, catalysts and electrolytic capacitors.

The whole field of etching has been reviewed by Lacombe^{30, 31} who includes other forms of etching, notably thermal etching. But in the context of electropolishing and anode behaviour Edeleanu^{32–34} may be considered to be the originator of electrolytic etching when he identified the value of potentiostatic control in this context for the etching of alloy steels. In such steels small changes in composition, due to segregation of chromium and nickel, can be exploited in simple solutions such as 20% H_2SO_4 at 25°C provided potential control is also available. The effect is illustrated in Fig. 11.9 where, on anodic polarisation, alloys containing more chromium and less nickel actively dissolve and passivate at less anodic potentials than

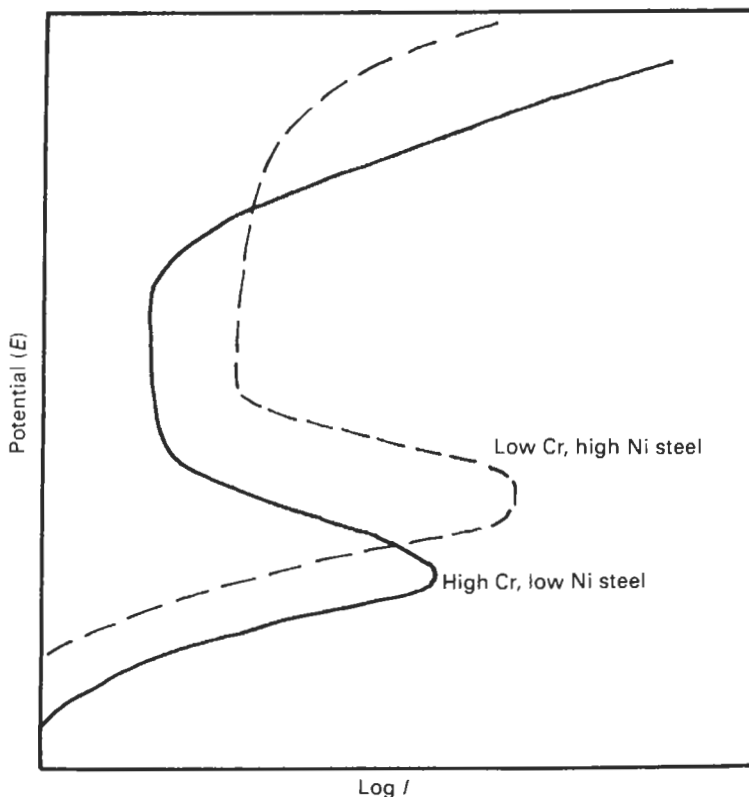


Fig. 11.9 Anodic polarisation behaviour for alloy steels (schematic)

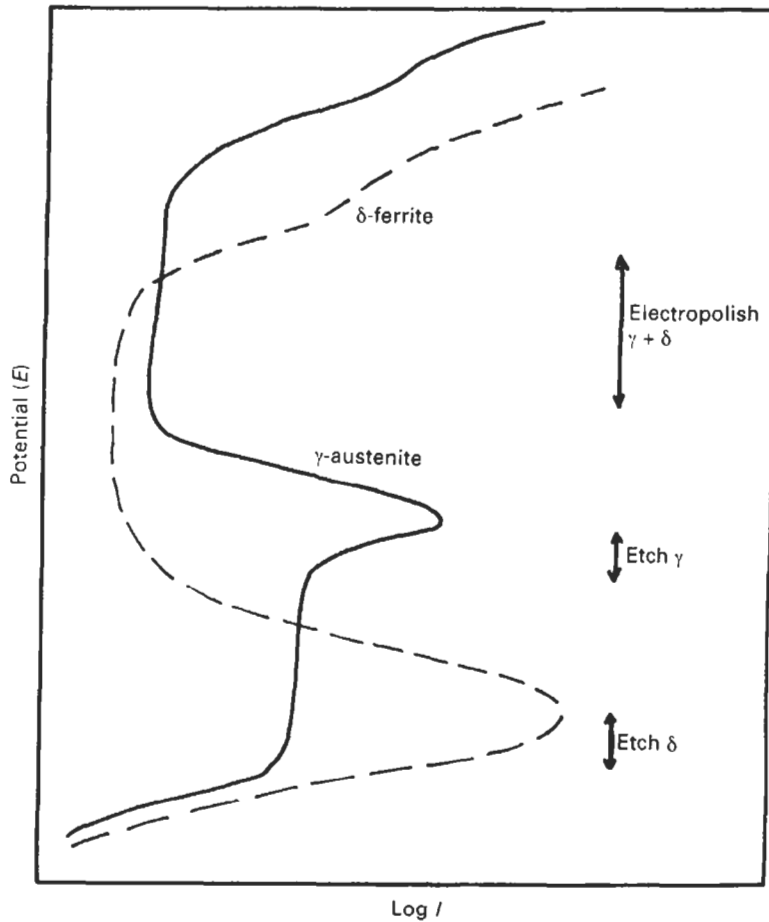


Fig. 11.10 Anodic polarisation of δ -ferrite and γ -austenite showing potential ranges for etching and electropolishing. Stainless-type steels in 5% sulphuric acid (after Cihal and Prazak³⁵)

alloys containing less chromium and more nickel; in a single alloy this could correspond to δ -ferrite and γ -austenite phases, respectively. This principle was immediately taken up by Cihal and Prazak³⁵ as a means of phase identification in alloy steels, and by others as a means of extracting selected phases from a complex alloy matrix for X-ray and electron microanalysis³⁶⁻⁴⁰. The effect for duplex stainless steels is illustrated in Fig. 11.10 in which anodic polarisation curves for γ -austenite and δ -ferrite are superimposed and selective etching potentials can be recognised. Figure 11.10 also shows how the concept of etch-polish behaviour arises whereby, by control of potential, one or all phases can be electropolished after which a shift in potential allows one phase only to be etched.

The selectivity of this etching procedure can be expressed quantitatively by a differentiation ratio with respect to one phase:

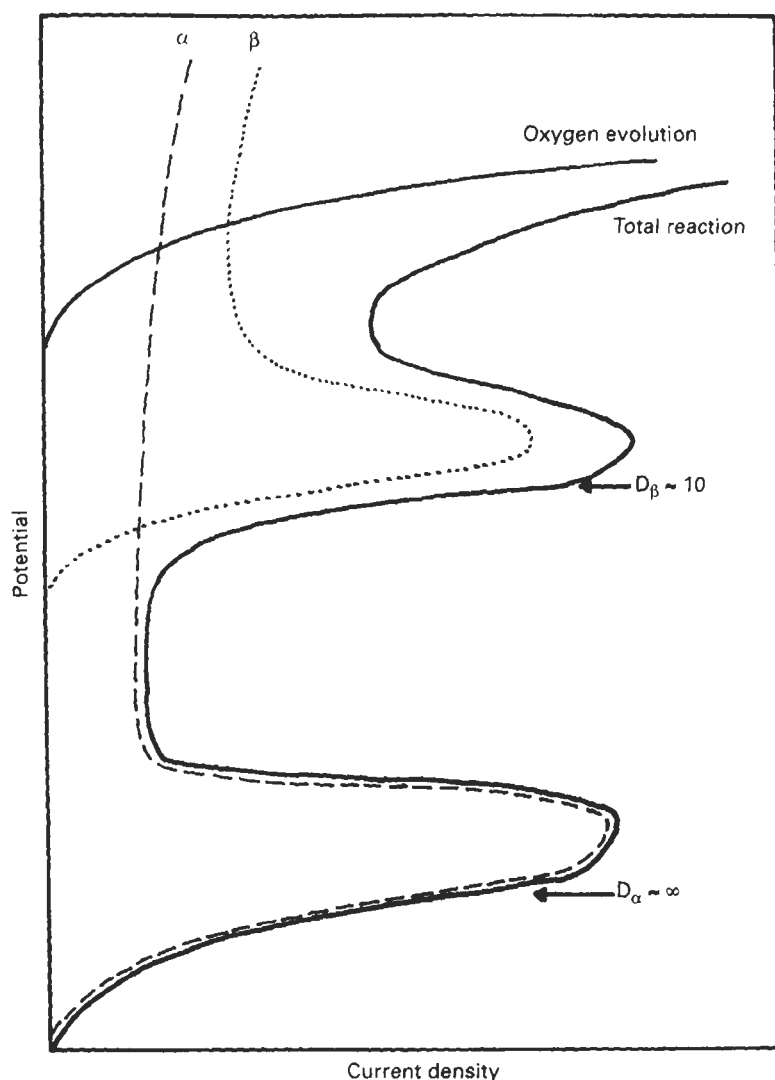


Fig. 11.11 Schematic polarisation curves for phases α and β showing the selection of optimum differential etch ratio conditions

$$D_\alpha = \left(\frac{i_\alpha}{i_\beta} \right)_E$$

where i_α and i_β are the individual anodic currents for phases α and β at constant potential which together give the total anodic current (Fig. 11.11). The ratio is independent of the proportion of the two phases, depending only on the dissolution currents. The best etching, and hence metallographic contrast, occurs when $D \gg 1$, an effect established for other alloys besides steels^{35, 41}.

For the more complex alloys anodic polarisation offers a vital extra variable in the use of selective etchants and has been widely exploited for alloys for which simple chemical etchants have proved inadequate. Besides many types of alloys steel^{32-40, 42-46}, this technique has been applied to copper and the Cu-Be-Ni-Zr alloys⁴⁷⁻⁵⁰, uranium-base alloys⁵¹⁻⁵⁴, Ni-Al alloys⁵⁵, tin-bearing invar⁵⁶ and many others.

Industrial Process Requirements

There are a number of special considerations when industrial-scale polishing processes are planned.

Plant

1. Processing utilises rack and jig techniques, and not barrels, in order to control low levels of agitation.
2. Tanks may be constructed of mild steel coated with rubber or plastics, lead, glass-fibre resin or stainless steel (316 or 317 type). Capacity is typically 100–1 500 l or 2 l per amp passed.
3. Heating should ensure temperature control to $\pm 1^\circ\text{C}$ and may be electric immersion heaters or steam coils.
4. Cathodes may be made of carbon, lead, copper or stainless steel.
5. Variable transformer/rectifier sets rated at 12–50 V and current sufficient to give 15–50 A/dm² supply d.c. power.
6. Agitation should be gentle and not severe, and is best achieved by busbar movement and not electrolyte flow or air bubbling.
7. Processing times of 3–10 min are usual, giving a total metal removal of 25–50 μm .
8. Good fume extraction and ventilation is needed because of the strong acids used. Fume washing may be necessary.

Processing sequence The following sequence is typical, although not all stages may be essential.

1. cleaning to remove oil, greases etc;
2. rinse;
3. pickling to remove scale;
4. rinse;
5. chemical and electrochemical polishing;
6. rinse;
7. desmutting post-treatment to remove gelatinous film;
8. rinse;
9. hot air dry.

Quality control Process quality control is concerned primarily with maintaining good process solutions and ensuring changing or make-up on depletion of acid or build-up of impurities, and ensuring good rinsing and drying to avoid staining of the finished product.

Product quality control relates to appearance and methods of assessing it either by subjective visual inspection or by objective tests such as reflectivity or surface roughness.

D. R. GABE

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11.4 Design for Corrosion Protection by Electroplated Coatings

Introduction

The use of electrodeposited metals to protect corrodible basis metals from their service environments has been well established for many years and accounts for by far the larger part of the activities of the plating industry. There are many reasons for using an electroplated metal finish in preference to an organic finish or to making the articles concerned from inherently corrosion-resistant materials.

Some of the reasons are aesthetic, and on many larger articles, such as motorcars, an attractive appearance is achieved by a careful visual balance between parts which are finished and protected by electroplating, and parts which are protected by organic finishes. In many other instances the manufacture of parts from corrosion-resistant materials is ruled out because of the relatively high cost of such materials, and in some cases the physical properties of the appropriate corrosion-resistant materials may render them either unsuitable for economic production or unable to perform the function for which the article is required.

Satisfactory service of an electroplated article is not achieved, however, unless adequate care is given to the choice of deposited metal, its thickness, the technique of application, and the design of the article. The choice of metal deposit is primarily determined by the basis metal, i.e. the metal from which the article is made, and the actual conditions to which the plated article will be subjected during service. In addition, however, attractive appearance and reasonable cost are also important considerations.

Deposit Thickness

Deposit thicknesses appropriate to various conditions of service are laid down in a number of specifications. Formerly, those of most general application were the standards issued by the British Standards Institution and listed in Table 11.6. These standards are still valuable documents, but those that have recently been revised now omit specific thicknesses of deposit and have

Table 11.6 British Standards for electrodeposited coatings

BS 1224	Electroplated Coatings of Nickel and Chromium
BS 1706	Electroplated Coatings of Cadmium and Zinc on Iron and Steel
BS 1872	Electroplated Coatings of Tin
BS 2816	Electroplated Coatings of Silver for Engineering Purposes
BS 3382	Electroplated Coatings on Threaded Components:
	Part 1 Cadmium on Steel Components
	2 Zinc on Steel Components
	3 Nickel or Nickel Plus Chromium on Steel Components
	4 Nickel or Nickel Plus Chromium on Copper and Copper Alloy (including Brass) Components
	5 Tin on Copper and Copper Alloy (including Brass) Components
	6 Silver on Copper and Copper Alloy (including Brass) Components
	7 Thicker Platings for Threaded Components
BS 3597	Electroplated Coatings of 65/35 Tin-nickel Alloy
BS 3745	The evaluation of results of accelerated corrosion tests on metallic coatings
BS 4290	Electroplated Coatings of Silver for Decorative Purposes
BS 4292	Electroplated Coatings of Gold and Gold Alloy
BS 4601	Electroplated Coatings of Nickel Plus Chromium on Plastics Materials
BS 4641	Electroplated Coatings of Chromium for Engineering Purposes
BS 4758	Electroplated Coatings of Nickel for Engineering Purposes
BS 5411	Methods of test for metallic and related coatings (14 parts covering various methods relevant to different attributes)
BS 5466	Methods of corrosion testing of metallic coatings (nine parts covering different methods)
BS 6137	Electroplated Coatings of Tin-lead Alloys
BS 6669	Methods of test for electroplated Silver and Silver Alloy Coatings

the format of 'methods of specifying' clearly laying out information which should be provided in order for electroplated finishes. Designers will find this information useful, but those seeking guidance on actual deposit thicknesses to specify will need to consult other experts, DEF standards or the earlier issues of British Standards. Standards require that the significant surface shall be specified, i.e. all that surface which must be covered with the minimum required thickness. In specifying the significant surface cognisance must be taken of the uneven distribution of electrodeposits around edges, corners and recesses.

The protection of screw threads by electroplated coatings presents peculiar problems arising from the geometry of threads and the components of which the threaded portion is a part. The first six parts of BS 3382 specify thicknesses which may be electroplated on to screw threads of standard form, dimensions, tolerances and plating allowances, without risk of interference on assembly and which will provide a degree of protection adequate for many purposes. Part 7 of BS 3382 is devoted to special methods of providing protection by electroplated coatings against more severe corrosive environments.

Deposit Distribution

An electrodeposited coating is never, in practice, completely uniform in thickness. The actual thickness of metal deposited at a particular point in a given time is dependent on the current density (i.e. the current per unit area) at that point, and the current density is not uniform over the whole surface

of a plated article—it tends to be highest at sharp points, edges and corners (see Fig. 11.12) and lowest in re-entrant corners and recesses (see Fig. 11.12*b* and *d*). Even a flat plate will not have a uniform deposit, since the current density will be higher towards the edges than in the centre, and highest of all at the corners (see 11.12*a* and *c*). Figure 11.12*d* shows diagrammatically the sort of deposit distribution which is experienced at a slot in a plane surface which has been plated.

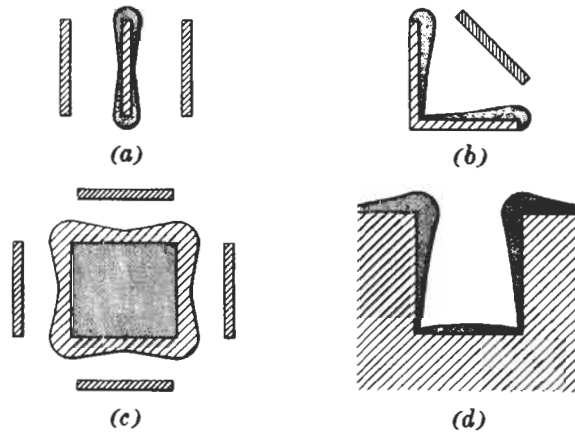


Fig. 11.12 Relation between current density and plating thickness

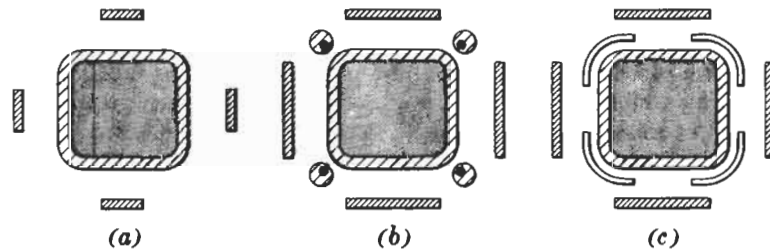


Fig. 11.13 Methods of securing more uniform current distribution

The distribution of current, and hence of the electrodeposited metal, can be made more uniform in several different ways. Sharp corners should always be avoided and curved corners used instead (see Figs. 11.13 and 11.14). In many instances plating anodes which conform approximately to the shape of the article being plated or which are suitable in size and carefully placed in relation to the workpiece will greatly improve the deposit distribution (see Figs. 11.13*a* and 11.15). Another method of effecting an improvement is to suspend 'burners' or 'robbers' near projections on the work to be plated (see Fig. 11.13*b*). These burners are electrically connected to the workpiece and take a high proportion of the metal deposited in regions of

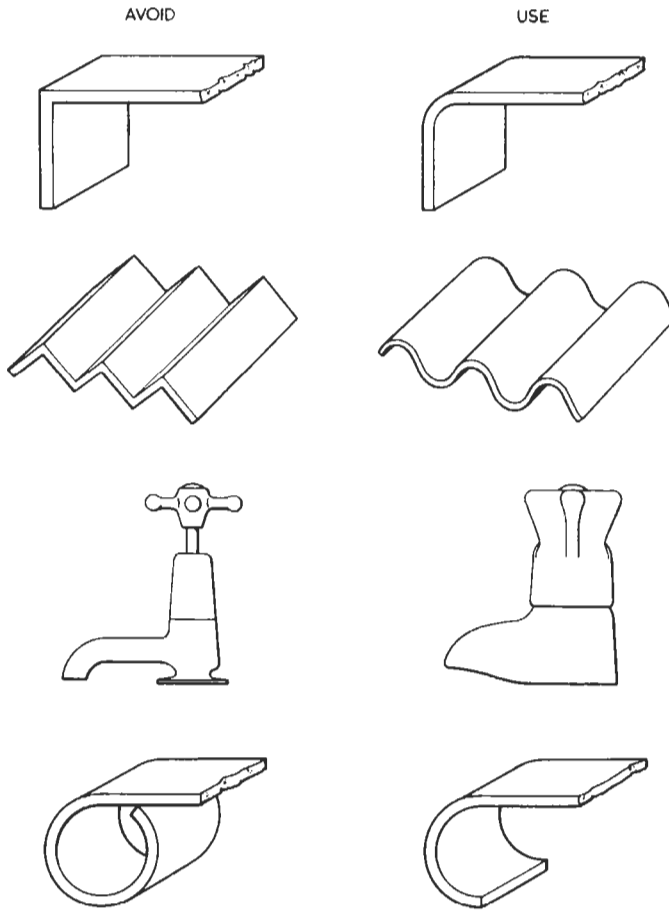
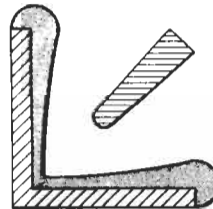


Fig. 11.14 Some design features which will lead to poor distribution and performance of electroplated coatings, and alternatives which will yield satisfactory results

high current density. Better than the use of burners is the use of plastics or other non-conducting shields (see Fig. 11.13c). These shields placed near projections which would otherwise be regions of high current density impede the current and solution flow to them and hence result in a more uniform distribution of current and deposited metal.

Fig. 11.15 Use of anode appropriate to the shape of the workpiece to improve current distribution



If conforming anodes or plastics shields are to be effective they must be fairly accurately located in relation to the workpiece. The practice, common in many plating shops, of wiring the work directly to the electrical bus bars over the plating tanks is, therefore, not satisfactory. Instead, the work should be mounted on rigid jigs or racks which are then suspended from the bars over the tanks.

Some electroplating solutions produce more uniform deposits than others, and the ability of a solution to deposit uniform coatings is measured by its 'throwing power' (see Section 12.1).

Design Considerations

Uniformity of Deposit

It is clear that for satisfactory service and resistance to corrosion, it is necessary not only to choose the right metal to be electrodeposited, and the right thickness of deposit, but also to ensure that the design of the basic article to be plated is such that a reasonably uniform deposit can be achieved without too much difficulty. The more complex the shape to be plated, the higher will be the cost, either because the total weight of metal over the whole article will have to be greater in order to provide the minimum thickness in the most difficult places, or because special plating jigs and anodes will be required to achieve a uniform deposit. The designer should therefore strive to avoid deep or narrow recesses, sharp edges and corners, sharp points, and generally complex shapes; he should aim to provide relatively simple shapes without sudden changes of contour or cross-section, and generous radii on all corners and edges, both external and re-entrant. Ideally, the worse the throwing power of the solution to be used for electroplating, the more simple should be the shape to be plated. Figure 11.14 illustrates some of the points mentioned. Recent studies^{1,2} have shown that the deposit distribution on complex shapes can be controlled much more predictably, but the designer should still aim for simplicity of shape as far as possible.

Surfaces other than significant ones The ease of achievement of a reasonably uniform deposit over the significant surface is, however, not the only way in which the design can influence the corrosion resistance of plated articles. Although the part of the surface which *must* be protected from corrosion is described as the significant surface, the remainder cannot be considered of no importance. Some protection must be given to such surfaces to prevent severe corrosion which might ultimately result in penetration of the article from the back. It can usually be arranged that a thinner deposit is plated on the less important surfaces while the full specified thickness is plated on the significant surface. An alternative method is to protect the less important surface after plating in some other way, e.g. by painting, if it is not possible to ensure an adequate thickness of plating without materially increasing the cost.

Physical properties The corrosion resistance of an electrodeposit depends not only on suitability for the service environment, thickness, and uniformity, but also on its physical and mechanical qualities such as adhesion to

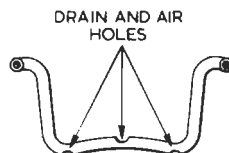
the basis metal, ductility, internal stress and porosity. All these properties depend primarily on the plating shop—the choice of processes, the skill and care of the operators and the exercise of proper control over the actual plating processes. The designer can, however, influence these factors to some extent, and can certainly help to make the plater's task easier. (The easier the plater's job, the more likely a satisfactory result is.) In order to ensure good adhesion of the electro-deposit to the basis metal, it is necessary to remove all grease, oxides and any other contaminants from the article to be plated³. This can be difficult with articles of very complex shape. Furthermore, the processes and solutions used for cleaning are usually different for different basis metals, and hence it is often not easy (and sometimes not possible) to clean satisfactorily an article assembled from parts made of different materials. It is preferable, therefore, to assemble such parts after plating.

High stress and low ductility of electrodeposited coatings are often the result of impurities in the electroplating solution. Such contamination of plating solutions is often the result of solutions being carried over from one process to the next in recesses and blind holes in work being plated. Contamination can also be caused in some cases by attack of the plating solution on parts of the article being plated which are not receiving a sufficient share of the total current to achieve an adequate deposited coating. This trouble can arise in deep recesses and holes, and particularly in the bores of tubes which are being plated externally (an extra anode running through the bore of the tube would be required to ensure a deposit inside). Tubes to be plated externally should always be rendered solution-tight if possible; alternatively provision should be made by suitably placed holes for easy rinsing and draining (see Fig. 11.16). Good platers, of course, purify their plating solutions at intervals to remove contamination, but any help designers can render in reducing the rate of contamination is obviously beneficial.

Articles of complex shape may be impossible to electroplate satisfactorily, and electroless nickel (see Section 12.5) may be useful in providing a relatively uniform protective coating. Even so, the considerations of access of cleaning and process solutions, and retention/draining of all process solutions, still apply.

Some porosity is inherent in thin deposits of certain metals, e.g. chromium, nickel and tin, but this usually disappears with increasing thickness. Porosity can also be caused by inadequate cleaning and by the condition of the surface of the basis metal, i.e. its degree of roughness, its porosity and the extent to which it is free from inclusions. Hence the designer can help by ensuring that the materials used for manufacture are of good quality and that machining is to a reasonable surface finish.

Fig. 11.16 Drainage holes in a tube to be plated externally



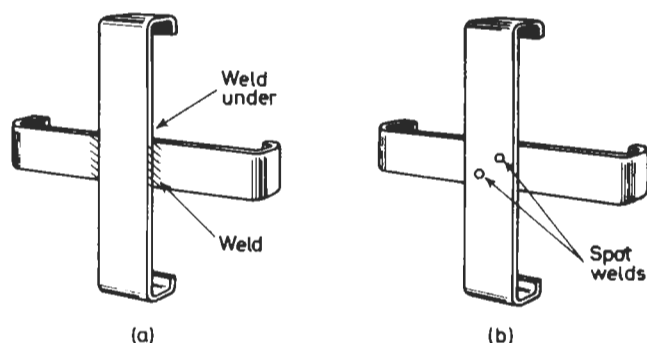


Fig. 11.17 Methods of joining straps. (a) Continuous welds prevent entrapment of process solution during plating and corrosive liquid during service, and (b) spot-welded joint leaves space in which process solution and corrosive liquids can be trapped

Retention of corrosive media Apart from their effect on deposit thickness, the construction and fabrication of plated articles can also influence corrosion resistance by affecting the retention of dirt and liquids in certain parts during service. Thus if two straps crossing each other have to be joined it is better that the joint should be welded along each edge (Fig. 11.17a) rather than made by riveting or spot welding (Fig. 11.17b). The latter arrangement allows process solutions to be trapped during plating, and rain, condensed moisture and dirt to be trapped during use. The closed welded joint of Fig. 11.17a avoids all these troubles. (Spot-welded and riveted joints are, of course, extensively used and often with satisfactory results. The point to be made is that for *maximum* resistance to corrosion they should be avoided.) Similarly, any form of ledge, cup or recess which could trap processing solutions and thus impair the quality of the plate, or which could trap dirt or corrosive liquids and hence lead to premature failure, should be avoided.

Reference may be made to BS 4479: *Recommendations for the Design of Metal Articles that are to be Coated*, Section 2 of which deals with electroplated coatings.

Conclusion

It will be seen that the design of articles to be electroplated can have a considerable effect on the corrosion resistance of the electrodeposited coating. The chief effects are the result of variations in deposit thickness, but also important are features which can influence the adhesion, porosity and physical properties of the deposit. Good design will also avoid features of the plated article capable of trapping liquids or solid contaminants which might cause more rapid corrosion.

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11.5 Design for Corrosion Protection by Paint Coatings

Introduction

Those in the construction industry often cast envious glances towards manufacturers of consumer goods, believing the latter allow for the coating operation when drawing up the plans for a new article. This is seen as being in sharp contrast with building a factory or power station. Here, with painting being the last operation and but a small part of the total budget, it gets little consideration from designers. That is the perception; in fact many industries remain guilty of not considering the effect of design upon the paint system. All too often sharp edges, acute angles and the like cause premature coating failures on articles as far apart as domestic radiators, earth moving equipment and structural steelwork. While these items are exposed to different conditions in use and in very different environments the reasons for their suffering paint detachment and substrate corrosion are often identical—design shortcomings preventing the even application of the coating at the specified thickness.

Since the second edition of this work there has been a quiet revolution in the coatings available to enhance the appearance of, and to protect, domestic equipment, cars, aircraft, structural steel, plant, etc. With many of these products improved performance is accompanied by intolerance to abuse during application. One thing remains unchanged: coating failure is blamed upon poor quality coatings or insufficiently skilled application. Rarely is the failure to design with coating in mind seen as the real reason for impaired product performance.

The design principles required to achieve the successful and economic use of coatings are identical for a wide range of surface treatments. This is reflected in BS4479:1990 which comprises nine parts covering methods of coating as different as electroplating and painting. It is further emphasised by removing the word 'metal' from the title, which now reads 'Design of articles that are to be coated'¹. The same principles are seen as common to all articles to be coated, irrespective of their basic composition.

The elementary design principles that must be followed, whether painting is part of a production line or undertaken on site, are considered in the

following pages. For convenience they are covered under the common application methods, e.g. 'Spray Painting'.

Coating is an integral part of the manufacturing process and designing with coating in mind is another. Coating is also of prime importance in maintaining coated items. Maintenance to retain the appearance and protection of the original coating by repainting should be recognised as an important design consideration—it rarely is.

Organic and inorganic paint systems are widely used to protect and enhance appearance because they are often economic and always flexible in use. In many industries paint is chosen when other coating processes are technically impossible or uneconomic. Because it is so often used upon subjects which are difficult to coat, sensible design detailing becomes even more important.

Finally, in considering coating it must never be forgotten that surface preparation is an essential part of the process and must also be considered by the designer.

Pretreatment Processes and Design

The processes are dealt with fully in Chapters 11, 14 and 15. Because many paint systems include an initial surface pretreatment, e.g. chromated aluminium or phosphated steel, BS4479:1990, Part 3 deals with conversion coatings and should be consulted by designers. Whatever the method of treatment, liquids must be able to drain quickly and freely from the surfaces. Crevices where liquids can become entrapped are best avoided. The surface configuration needs to be such that active solutions can be washed away, leaving the surface to be painted completely free from unreacted pretreatment solution. Failure to achieve the requisite level of freedom from the surplus chemicals causes paint failure, e.g. osmotic blistering.

Spray Painting

There are three main processes:

1. high pressure air spray (usually called 'conventional spray');
2. airless spray;
3. electrostatic spray.

In considering design the first two can be reviewed together.

Conventional and Airless Spray

In conventional spraying paint is forced under pressure to the spray gun, where it mixes with air and, forced through a small orifice, atomises. Airless spray is created by forcing paint at extremely high pressures through an accurately designed small hole. Rapid expansion as it leaves the gun produces an extremely fine and very even spray pattern. No air is mixed with the paint before it leaves the gun, so avoiding 'dry spray'. A wetter, heavier

coat can be applied, giving better coverage of sharp edges and faster working than can be achieved with conventional spray.

Either system can be used manually or as part of an automated plant. Many modifications of the basic spray guns are available, widening the engineer's potential choice of designs. Some equipment allows paint to be sprayed hot, facilitating the application of very thick coats.

Design Considerations

1. Despite the ability to adapt spray painting techniques to cope with a multitude of shapes and sizes, all surfaces must be accessible for painting (and indeed for preparation). It is worth remembering that high output spray equipment is infinitely more cumbersome than the smaller set-ups used in laboratories. Thus, fins and ribs must be well-spaced with their edges made round and smooth to retain paint more readily.
2. Sulphates and chlorides are present in industrial and marine atmospheres. In water they accelerate the corrosion of steel. Avoiding lodgement areas for water and dirt reduces the risk of the latter acting as a poultice in which the corrosive salts can build up.
3. Sharp edges should be avoided and external angles given at least a 1.0 mm radius. Where indentations are unavoidable, their edges should be rounded to a radius of about one-quarter of the depth.
4. Spot and intermittent welding produces crevices in which corrosion begins and dirt builds up. These types of welding also create difficulties with the surface preparation required before paint is applied. Continuous welds are better.
5. Countersunk rivets or screws give a surface profile which is compatible with painting; protruding bolts and rivets are very much more difficult to coat adequately. Welded joints can aid optimum shaping for painting. Butt joints are preferable to lap joints.
6. The responsibility for dealing with surface defects is frequently hotly debated *following* a coating failure. The designer should specify what is required. Notable examples are weld grinding, the removal of weld metal spatter, welding residues, burrs, etc. All of these need to be dealt with before surface preparation for painting is begun. Surface pinholes must be avoided and machining marks minimised if sound, aesthetically acceptable coatings are to be produced.

Electrostatic Spray Painting

This method is used increasingly for the factory finishing of a wide range of articles. Portable units are also used for repainting items as large as Concorde! Electrostatic painting is rarely if ever used by the construction industry under site conditions. The principle is straightforward. The item to be painted is earthed and the paint electrically charged. The charged paint particles are attracted to the earthed object, wrapping themselves evenly around it. This allows the back and front of the article to be coated simultaneously. A reduction in overspray allows significant savings in the volume of material used.

The method has one major disadvantage—its inability to coat internal angles and the like. ‘Air assisted’ electrostatic spray guns are available and do overcome this deficiency to some extent.

Design considerations Those listed above under ‘Spray Painting’ are all relevant. To them can be added two more:

1. Avoid cavities and recesses because this application process does not coat the inside surface of an article adequately. Where they are essential elements of the design consider using a different application method.
2. Electrostatic attraction produces a build-up of paint on the edges of holes and slots, causing runs and sags. Such features on visible surfaces are best avoided. If this is impossible, other application methods should be researched.

Dipping

Dipping plants range from a simple tank in which the paint is occasionally stirred by hand to complicated set-ups where paint is circulated and its constants monitored automatically. The actual method remains the same. The article is submerged in the paint, then raised and hung over the tank or a drainage area to allow surplus paint to drain off. The process has inherent disadvantages which are:

- (a) Paint may be held in pockets or depressions and not drain off.
- (b) Complicated shapes give uneven coverage, which produces sags and runs.
- (c) Paint on edges may be over-thick; tears can occur on corners.
- (d) Gaps and threads can be bridged and holes blocked.
- (e) Refluxing or solvent washing may take place in sections where access for paint is restricted, washing off the paint.
- (f) Paint drains downward and the film thickness is therefore always greater at the bottom of the article.

A variation of dipping suitable for small items is barrel painting or ‘tumbling’. A cylindrical or octagonal barrel is loaded with the articles to be painted plus a small amount of paint. The barrel is rotated until the items are completely coated, when they are removed for drainage and drying.

Design considerations

1. Correct jiggling and the suitable positioning of holding points are essential to obtain speedy and effective drainage.
2. Paint traps should be avoided, e.g. close bends of 180°, and rolled and bent edges. Drainholes should be located low down in hollow articles.
3. Large articles require enough holes of the requisite size to ensure swift immersion.

Electrophoretic Coatings

The process utilises water-thinnable paints which are diluted to a much lower viscosity than paints used in dip tanks.

Paints are specially formulated for one of two processes. In the first, anodic electrodeposition, the article to be painted is made the anode in a d.c. circuit. Cathodic electrodeposition is the reverse operation. The process takes place under carefully controlled conditions in a tank. Current passes through the paint causing it to deposit uniformly over the article in a uniform film whose thickness can be accurately controlled. The paint film is insoluble in water and exhibits remarkable adhesion after stoving. Electrodeposition is widely used to apply primers, e.g. by car manufacturers, and one coat finishes.

Advantages over dipping are numerous: there is no sagging and no blocked threads or holes; the cover on edges, welds and seams is superior; box sections are uniformly coated; Coating of mixed components is possible, with virtually 100% paint usage; and, above all, because the paints are water-borne, there is no necessity for flash off zones or fire protection.

There are a few disadvantages: plant installation cost is high; only one coat can be applied by this process; substrate imperfections are mirrored.

Design considerations

1. The metal pretreatment process requires careful selection, particularly with the cathodic process. BS4479:1990, Part 3, 'Recommendations for Conversion Coatings' should be consulted.
2. An electrical connection point is required.
3. The placing of jiggling points is particularly important to ensure adequate drainage, to allow gas to escape and, to avoid air entrapment.
4. The positioning of access and drainage holes in box sections requires careful consideration. Elsewhere hole positioning is less important, although an unobstructed current path is advisable.

Powder Coatings

Pigmented resins are applied as dry powders and then fused by heating to 220°C or higher. The process is effective with lightweight metal components and pipework. It is likely to remain uneconomic for use on heavy sections, e.g. hot-rolled steel universal beams and columns.

Thermosetting and thermoplastic powders are available. The former are usually applied by electrostatic spraying or induction line processing and the latter by a fluidised bed technique. Thermoplastic powders can produce coatings up to 3 mm thick. With thermosetting varieties 100 μm is usual, although greater thicknesses are possible. Powder coatings can provide toughness, and impact, abrasion and weather resistance.

Design considerations

1. Very high standards of surface preparation are necessary, e.g. abrasive blast cleaning to Sa2½, BS7079: Part A1, 1989 for steel components

which will be exposed in aggressive environments. This is usually followed by a chemical pretreatment. The restrictions imposed upon the design by these two requirements must not be ignored. BS4479:1990, Part 3 is relevant to designing for chemical pretreatment.

2. Dissimilar metals should be avoided.
3. It is wise to discuss methods jointly with the powder coating applicator. First, the materials used must withstand temperatures of circa 220°C. Second, some commonly used jointing materials are incompatible with all pretreatment systems.
4. The surface condition of the object to be coated requires specifying extremely carefully if a high standard of finish is required, because powder coating tends to faithfully reflect surface contours and blemishes.
5. Welds require grinding prior to surface preparation.
6. Galvanising should be post-fabrication, with steel sheet treated to BS2989³ and other items to BS729⁴. Where appearance is important, designers could do worse than have galvanised samples coated before deciding whether powder coating will produce required standard.
7. All coating should be post-fabrication, cutting or drilling coated sheet or tube is unacceptable. However, coated items can be bent or formed.

Painting by Brush and Roller

In the industrial world of manufacturing plants, power stations and the like, more than 80% of painting is concerned with the maintenance of existing structures and plant. Although airless spraying can be more than 20 times faster than brush application and conventional spray some four times as fast, there are many occasions where access difficulties and safety considerations prevent their use. Rollers and brushes therefore continue to be widely used.

Rollers are available up to 450 mm wide and are at their best on large unbroken surfaces, e.g. storage tanks, pipework etc. when application rates two to three times faster than brush application are achieved. Long-pile (up to 30 mm long) rollers are particularly useful on rough or pitted surfaces.

The largest brushes commonly used on industrial steelwork are 100 mm wide. While their use is slow and laborious on large areas, they are able to reach otherwise inaccessible areas. The painter requires no more than a 5 l container of paint to fuel his brush for up to 8 h. This container size can be handled when working at height. The trays and buckets used with rollers are less easily handled.

Design considerations The general requirements set out above under 'Spray Painting' are apposite. Additionally designers need to remember the following points:

1. Rollers do not coat edges or internal angles adequately, nor are they particularly efficient on welds. Such areas should be stripe-coated after surface preparation is completed and prior to repriming overall.

2. Neither roller nor brush is capable of attaining the same film thickness as airless spray. A paint which consistently gives $100\text{ }\mu\text{m}$ dry-film thickness when applied by the latter means is unlikely to produce more than $75\text{ }\mu\text{m}$ d.f.t. comfortably by roller or brush; the more complex the geometry of a structure the more unlikely it is that consistent results will be obtained.
3. Tubular structures are easier to coat than those produced from profiled metal, e.g. a flare stack constructed of welded tubes can increase the life of a brush- or roller-applied paint system by as much as four times over the same process applied to a similar structure built of welded angled steel.

The Effect of Surface Profile

Most paints, excluding a few in the 'high performance' category designed for painting jetties and the like, contain solvents which evaporate as the film is formed. A paint at 15% volume solids dries to a mere $15\text{ }\mu\text{m}$ given that the wet coat measured an even $100\text{ }\mu\text{m}$. Its ability to hide surface imperfections is minimal. For many items, finishers can no longer afford the luxury of multicoat systems incorporating fillers and stoppers which have to be carefully abraded to a plain surface. Although two-pack fillers are available which are formulated for direct application to metals, they cannot be easily used when sophisticated pretreatments are an essential part of the corrosion-inhibiting process. Nor is their use over pretreated and primed metal feasible in any but those systems where the cost of painting is negligible in comparison with the total capital outlay. Coatings applied by dipping, electrostatic spray and electrodeposition all tend to mirror the surface, leaving imperfections clearly visible. Aesthetic considerations apart, these flaws are lodgement areas for water, dirt and chemical contaminants — points at which coating breakdown and corrosion are likely to begin. It is imperative that the characteristics of the coating and the weaknesses of the various application methods are carefully evaluated when the likely surface finish of the manufactured article immediately prior to painting is known. It may be necessary to spend a little more upon dressing the surface to ensure good paint performance. Alternatively a change of paint system or application method could be a better answer.

Blast cleaning is a widely used preparatory method for the steelwork of bridges, factories (particularly exterior steel and process plant), offshore installations and the like. This treatment produces a profile and it is vital that the bare metal is adequately covered by the primer and subsequent coats. Each coat of the paint system requires matching to the likely profile on the blasted steel to ensure the total system is able to attain its designed life in the environment in which it will be exposed. For example, if a profile produced by shot blasting is considered to be 'medium' when viewed against a surface profile comparator complying with ISO Standard 8503 Part 1, then the peak-to-trough distance of the profile should lie between 35 and $60\text{ }\mu\text{m}$, while the values for a 'medium' profile produced by grit blasting and judged in the same way will be 50 to $85\text{ }\mu\text{m}$. The lower peak-to-trough distances and the higher limit of the profile produced by shot blasting are

unlikely to be critical if the designer has chosen a 50% volume solids primer which can be applied at 150 μm wet to produce a dry film thickness of 75 μm . However, if with the grit-blasted profile the maximum 85 μm predominates, the primer might provide insufficient protection over the peaks in the profile. Specifying a second priming coat if in doubt is always wise.

Acknowledgements The author gratefully acknowledges the contributions from BSI PVC/27 members and the help of the British Standards Institution staff.

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12 METHODS OF APPLYING METALLIC COATINGS

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12.1 Electroplating

Approach¹⁻⁷

There are books and reviews dealing with electroplating which approach it as a commercial technology, a useful art or an interesting process for scientific enquiry. In this case the emphasis is on the production of coatings for the control of corrosion and the consequences for service corrosion of events at various stages of electroplating. Corrosion control is not the sole function of electroplated coatings; indeed most authors play down corrosion in favour of 'more positive' virtues such as decoration (sales appeal), reflectivity, wear resistance, solderability or low contact resistance. However, to preserve these properties it is essential to prevent corrosion; in essence, electroplated metal coatings are required to confer corrosion resistance *together* with one or more other property, the nature of which provides the criteria on which selection of a coating is made. Corrosion protection is a common factor.

Origin⁸⁻¹⁶

The production of electricity by metallic corrosion in Volta's pile (1786) was followed by the reduction of metal ions to metal by electrons at a metal/solution interface. Electroplating is an application of electrodeposition to produce thin, coherent, adherent coatings of solid metal, and is one of the important methods for producing coatings. Brugnatelli⁹, a Professor of Chemistry at the University of Pavia, published an account of silver plating in 1800, and is said to have gold plated silver coins using Volta's pile as early as 1805. Wollaston deposited copper (presumably a very small quantity) on silver wire using current from an electrostatic generator. Electrodeposition was developed energetically in the succeeding three decades, and by 1840 commercial electroplating had advanced to the stage where patent protection was being sought for various processes. The main source of electricity for the first six or seven decades was the primary galvanic cell, and progress was aided by the invention of cells such as those of Daniell, Meidinger, Grove and Bunsen, which were capable of delivering large currents for long periods without polarisation. Faraday discovered electromagnetic induction in 1831 and Pixii used the commutator in 1832 to produce a direct current generator, but it was not until about 1870 that several independent inventors used electromagnetic field coils to generate the heavy

currents needed for electrolysis. Large scale electroplating enterprises were established by the latter part of the 19th century. In 1883 the Postal Telegraph Company of New York used 200 copper plating cells to deposit 250 kg/d onto steel wire. Aqueous solutions have always been by far the most important electrolytes. There have been many investigations of non-aqueous solutions or ionic melts, and Davy deposited the alkali metals from the latter in 1807. Aqueous solutions, and their associated pre- and post-plating treatments are so well established that they are likely to remain pre-eminent for the immediate future.

Substrates

Metallic substrates which are good electron conductors and non-metallic ones which are not, can both be electroplated with adherent coatings, but the preliminary procedures or 'pretreatment' differ markedly. The commonly plated metal substrates are mild and low-alloy steels, zinc alloys for die-casting, and copper or high-copper alloys like brasses, bronzes and beryllium coppers. A large number of other alloys can be electroplated, but their use is restricted to particular industries, and they often require special pretreatments. Aluminium alloys, stainless steels, titanium alloys and refractory metals are examples. The three major substrates are plated with corrosion control as one of the important objects, but with less common substrates this may not be the case. There has been a rapid growth in electroplating parts made from plastics material. The main object is to make the part look metallic for reasons of appearance rather than function. A complicated acrylonitrile-butadiene-styrene copolymer dispersion (ABS) was the first plastics material to be plated on a large scale. It has been followed by polypropylene, and the development of plating grades of other plastics (e.g. polysulphone, polycarbonate, epoxide resins, glass-reinforced polyester) is in hand. Metallic corrosion problems arise as soon as plastics have been plated, creating a new field for the corrosion enthusiast to investigate.

By exercising ingenuity, most non-conducting objects may be electroplated, and this is a long-established small-scale operation. The usual aim is artistic or a search for novelty, a good example being the preparation of a heavily gold-plated haggis for the 1973 conference of the Institute of Metal Finishing which took place in Edinburgh.

Pretreatments

Metallic Substrates¹⁷⁻²¹

This is considered in detail in Chapter 11, but a brief review is relevant here in relation to electroplating.

Metallic articles arrive at the electroplating stage with a surface film of *soils* derived from earlier production processes. These are divided into three classes:

- (a) Organic films, oils, greases and perhaps polymeric films.
- (b) Fine particles suspended in (a), often of siliceous material, i.e. *dirt*.
- (c) Films of the substrate oxide or other corrosion product.

With few exceptions it is more efficient and economical to use at least two different pretreatments, i.e. *degreasing* processes which deal with (a) and (b), and *pickling* processes which remove oxide and corrosion films. Degreasing comes first, as pickling processes fail on hydrophobic surfaces.

Degreasing Hydrocarbon or mineral oils are removed by solvents; *vapour* degreasing with chlorinated solvents, or emulsification, are common alternatives. Greases of animal or vegetable origin, which are fatty acids, alcohols or esters, are removed with hot aqueous solutions of high pH (*alkaline* degreasing). They react with alkali to form water-soluble soaps. Electrolytic alkaline degreasing is considerably faster than soak cleaning. The work, immersed in hot alkali, is usually the cathode. A mass of hydrogen bubbles formed at the solution-metal interface undermines and removes the grease very effectively; saponification takes place more slowly later. Ferrous metals may be degreased anodically, the metal surface becoming passive, but non-ferrous metal anodes corrode in hot alkaline solutions. Anodic cleaning produces only half the volume of gas (oxygen) and is less effective on that count. There is however an advantage. During use small amounts of metal enter the cleaning solution; other metals enter as impurities in the salts and make-up water. A thin metal film may be electrodeposited during cathodic cleaning, which if it remains can decrease the corrosion resistance of the main deposit. Anodic cleaning avoids this danger even when the cleaning bath is contaminated. For steel, and occasionally for copper alloys, a cleaning cycle is employed, with the work cathodic for degreasing but reversing the current for the final few seconds, during which any thin film of impurity metal is removed by anodic dissolution.

Alkaline cleaning solutions are compounded from sodium hydroxide, trisodium phosphate (TSP), sodium silicate, sodium carbonate, soaps and detergents, and other materials. The higher the pH the more effective is saponification, but with non-ferrous metals the greater is the danger of corrosion. Zinc diecastings and aluminium need much less aggressive alkalies than are safe with steel. For aluminium and its alloys a high concentration (10%) of sodium silicate acts as a corrosion inhibitor and a cleaner.

To check the efficacy of grease removal, the alkali solution is rinsed away or neutralised by dipping in dilute acid. If, after removal from the acid, the draining metal surface remains wetted evenly all over for 30–60 s (or until it dries by evaporation), hydrophobic soils have been removed. Traces of grease cause the surface to de-wet, and surface tension draws the water into separate droplets. This is the *water-break* test. Traces of grease which remain when the work is plated do not prevent electrodeposition, but are detrimental to adhesion and corrosion resistance.

Particulate dirt is usually removed together with the grease which binds it, although there are a few exceptions. Sheet steel may carry a 'smut' of finely divided carbon (or perhaps iron carbide) left from pickling processes in steelmaking. This is not removed with grease, and if evenly distributed is not apparent until the work is rubbed locally. Left in place it leads to porous and poorly adherent coatings. Whilst it can be removed by mechanical means, e.g. vigorous brushing, this is impracticable when automatic plating machines are used. Steel which shows this defect may be unsuitable for plating.

Removal of oxides and corrosion products Oxide and corrosion-product films are removed by dissolution in aqueous solutions. Hydrochloric and sulphuric acid are the most common. Concentrations and temperatures are varied according to the substrate. For mild steel, for example, cold 15 wt% HCl is suitable, but for zinc diecastings the concentration must be reduced to 0.25 wt%, and the pickling time must be kept very short to avoid excessive attack. Rust is more quickly removed by acid pickling when in the prior degreasing stage the work is made the cathode, than when it is the anode. Cathodic cleaning partially reduces rust to magnetite and iron, which undergoes rapid reductive dissolution in the acid. Mixed acids containing wetting agents are supplied as proprietary mixtures; hydrochloric, sulphuric and phosphoric acids are common. Inhibitors—generally amino compounds—may be added, but strongly absorbed films of inhibitors or their breakdown products may cause trouble later. Electrolytic pickling is used for special purposes, but hydrochloric acid is unsuitable for this purpose because of its volatility and the possibility of chlorine evolution. Cathodic pickling of steel in 10–20 wt% sulphuric acid enables thick rust or scale to be dissolved without losing metal, which is cathodically protected. Anodic pickling in 42 vol% (about 55 wt%) sulphuric acid is used to remove a thin surface layer from steel. A high current density is used and dissolution, which is under diffusion control, is uniform. After 10–20 s the metal becomes passive and dissolution ceases. Disordered and fragmented metal produced by abrasion or machining is removed to leave a surface which favours good adhesion of an electrodeposit. Oxide and corrosion products on copper and its alloys may be removed in hydrochloric or sulphuric acids, less concentrated than used for steel. Sulphuric acid allows the dissolved copper to be recovered and the acid to be regenerated by electrolysis. However, when copper alloys are cathodically degreased, cuprous oxide is reduced to loose copper particles which do not dissolve in acid. An electroplated coating over loose metal is likely to be defective. A much more aggressive mixture of sulphuric and nitric acids known as a *bright dip* or sometimes (wrongly) *aqua fortis* is used. This is a rudimentary chemical-polishing system and produces a bright surface from which the loose particles have been removed.

Non-conductors ^{22–32}

Plating plastic articles has become a widespread commercial process fairly recently. The main plastics in use at the time of writing are ABS and polypropylene. Both replace diecast and pressed metal in various fields. Moulded parts have smooth surfaces unsuited to producing adherent plate, and the first step is to 'etch' the plastic surface by using strongly oxidising acids, usually chromic plus sulphuric acid mixtures. The plastic must have dispersed in its surface small areas more susceptible to oxidation than the surrounding matrix, and these are introduced in a variety of ways during manufacture. Etching produces a pattern of small pits. The second step is to produce within the pits and over the surface a fine metallic precipitate. One method is to dip in solutions of stannous and palladium salts in succession, which produces fine palladium particles, but there is a variety of proprietary processes available. The metal particles become nuclei for the

deposition of a metal coating from an electroless plating bath (see Section 12.5). This is an aqueous solution of a metal salt containing a reducing agent that is able to reduce the metal ions to metal. The solution is unstable but is compounded and used so that homogeneous electron transfer does not occur, and there is neither homogeneous precipitation of metal, nor heterogeneous precipitation on non-conducting surfaces but only on the metallic nuclei on the plastic surface. Several electroless plating processes have been devised but only those for copper or nickel are widely used for plastics. Once a continuous coating of metal has been produced, the substrate can be transferred to an electroplating bath for the application of any desired coating. Most plastic articles are finished with nickel and chromium.

Mechanical Pretreatments³³⁻⁴⁰

Mechanical processes which cold-work a substrate have important effects on electrodeposits. Examples are grinding and abrasive polishing, grit and shot blasting, cold rolling and severe cold deformation. They alter the metallurgical structure of the substrate, reducing the surface grain size and in some cases produce small crevices filled with non-metallic debris. Abrasive processes which act parallel to the surface (e.g. grinding, polishing) may leave splinters and leaves of metal attached at one end but otherwise separated from the surface on which they lie. In addition, non-metallic abrasive material is embedded in the surface. Surfaces which are neither annealed nor otherwise treated to remove mechanically disturbed surface layers affect the structure and properties of metal electroplated over them, as mentioned below. In many cases one result of the modification of the electrodeposit is to reduce the corrosion protection it affords. Where the same topographical alteration of a substrate can be achieved by non-mechanical means, e.g. electrochemical polishing, electrochemical machining, chemical milling, the surface left is not cold-worked and does not disturb an electrodeposit to the same extent.

Plating Processes

Electroplating⁴¹⁻⁴³

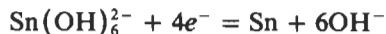
The metallic substrate, clean and rinsed, is immersed wet in the plating cell. The base metals which are usually plated present an essentially metallic surface to the electrolyte, and the slight corrosive action of the rinse water in preventing the formation of any substantial oxide film is important. A critical balance of corrosion processes in the initial stages is vital to successful electroplating, and for this reason there is a severe restriction on the composition of the electroplating bath which may be used for a particular substrate. This will be discussed later. The substrate is made the cathode of the cell; it may be immersed without applied potential ('dead' entry) or may be already part of a circuit which is completed as soon as the substrate touches the electrolyte ('live' entry). Live entry reduces the tendency for the plating electrolyte to corrode the substrate in the period before the surface

is covered by the coating. The main cathodic process is usually the reduction of dissolved ions to metal in the form of an adherent, coherent coating.

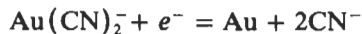
The ions reduced may be aquo cations, e.g.



or oxyanions, e.g.



or complex ions, usually cyanides, e.g.



Cations are assisted by the electric field to migrate to the cathode. On the other hand, the field impedes the migration of anions, and diffusion has to overcome this. It is rare for metal reduction to be the sole cathode process, since water and other dissolved substances are reduced simultaneously. Many compounds are added intentionally to take part in the cathode process, with the object of modifying the nature of the coating. Such materials are called *addition* agents and are subdivided into classes based on their main effect (e.g. brighteners, levellers, grain refiners, stress reducing agents). In all aqueous solutions, water may be reduced:



This reaction becomes thermodynamically possible whenever the cathode potential falls below

$$E = + \frac{RT}{2F} \ln \frac{a_{\text{H}_3\text{O}^+}^2}{\bar{P}_{\text{H}_2} a_{\text{H}_2\text{O}}^2} \quad (12.1)$$

Where R is the gas constant, T the temperature (K), F the Faraday constant and \bar{P}_{H_2} is the relative partial pressure (strictly, the fugacity) of hydrogen in solution, which for continued evolution becomes the total external pressure against which hydrogen bubbles must prevail to escape (usually 1 atm). The activity of water $a_{\text{H}_2\text{O}}$ is not usually taken into account in elementary treatments, since it is assumed that $a_{\text{H}_2\text{O}} = 1$, and for dilute solutions this causes little error. In some concentrated plating baths $a_{\text{H}_2\text{O}} \neq 1.0$ and neither is it in baths which use mixtures of water and miscible organic liquids (e.g. dimethyl formamide). However, by far the most important term is the hydrogen ion activity; this may be separated so that equation 12.1 becomes

$$E = - \frac{RT}{2F} \ln \bar{P}_{\text{H}_2} a_{\text{H}_2\text{O}}^2 - \frac{2.303 RT}{F} \text{pH} \quad (12.2)$$

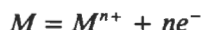
$$\text{As } \bar{P}_{\text{H}_2} \approx a_{\text{H}_2\text{O}} \approx 1, \text{ we have at } 298\text{K}, E \approx -0.059 \text{ pH} \quad (12.3)$$

These considerations have been based entirely on thermodynamics and take no account of the overpotential, which is dependent on the rate of the process and the nature of the surface at which the reaction occurs. For this reason, the rate of reduction of H_3O^+ or H_2O is usually low, and remains so to potentials from 0.5 to 1.0 V below that given in equation 12.1. Even so, the instability of water is an insuperable obstacle to electrodeposition

metals whose ions are so stable in aqueous solutions (e.g. Al^{3+} aq.) that water reduction becomes the sole cathode process (see Section 20.1 for the kinetics of the hydrogen evolution reaction).

Much time has been given in recent years to studying the mechanism of electrodeposition. Most investigators have assumed that electrodeposition should follow a mechanism akin to that for the deposition of a crystalline coating by condensation of a vapour. The solvated metal ion approaches and adsorbs on the cathode, losing some of its solvation sheath as the cathode gains the requisite electrons. The *adion* which is mobile, diffuses over the cathode surface until it reaches an atomic step. It adsorbs on the step, losing more water of solvation, and having its freedom reduced to diffusion along the step. Further desolvation and co-ordination follows when it reaches a kink in the step, at which stage it is immobilised. When other adions following this path eventually join and submerge the first, co-ordination with water in the electrolyte is exchanged fully for co-ordination with metal ions in the metallic lattice. This view of the mechanism of electrodeposition is plausible and compatible with both current views on metallic crystals and their defects, and certain properties of electrodeposits. It is, however, a preconceived notion, and considerable experimental difficulties in the way of producing evidence are responsible both for the numerous different investigations in the field, and for the fact that the evidence produced is impressive more for its volume than its conclusive force.

Current enters through the metal-electrolyte interface of the anode, which is usually made from the same metal as is plated on the cathode. The anode dissolves replacing the metal lost at the cathode:



The overall process is metal transfer from anode to cathode via the solution. The form of anode corrosion is important, and materials may be added both to the anode metal and to the electrolyte, to influence it. There are important instances where an insoluble anode is used, and the anode reaction becomes the oxidation of water or hydroxyl ions:



and also the oxidation of any other susceptible materials. Oxidation of water may occur at an anode which was intended to be soluble, if the metal becomes passive. The minimum potential above which the anode must rise before oxidation of water occurs, is:

$$E = E^0 + \frac{RT}{4F} \ln \frac{\bar{P}_{\text{O}_2} a_{\text{H}_3\text{O}^+}^4}{a_{\text{H}_2\text{O}}^6} \quad (12.4)$$

In this equation E^0 is the standard electrode potential of the water/oxygen reaction, i.e. $-\Delta G_{\text{H}_2\text{O}}^0/nF$. Simplifying, equation 12.4 at 298K becomes

$$E = 1.23 - 0.059 \text{ pH} \quad (12.5)$$

There is often an overpotential of about 0.5 V before the rate of oxidation of water becomes rapid.

Aqueous Electrolytes⁴⁴

Aqueous solutions have a complex structure. Liquid water is anomalous; properties estimated by interpolation from those of neighbouring hydrides in the periodic table fall wide of the observed properties. For example, estimated melting and boiling points are -43°C and -11°C , respectively. Molecular interaction (hydrogen bonding) imposes short range order in the liquid, which the anomalous properties reflect. Some of the crystal structure of ice is retained in the liquid, though the structure is less open, and water shares this peculiarity with diamond, silicon and germanium, since in each case the liquid is denser than the solid at the melting point. A simple view of water is as a fluid with two species, small local regions with an ice structure and others with a strongly associated but irregular structure $(\text{H}_2\text{O})_n$. The 'icebergs' and random groups are in dynamic equilibrium, exchanging individual molecules throughout the lifetime of the larger groups, which are not themselves permanent.

Water has a permanent dipole moment (strictly it is a quadrupole moment) caused by the asymmetry of the molecule and the greater electron affinity of oxygen. When soluble strong electrolytes, e.g. nickel sulphate, dissolve they dissociate completely, and the interactions between the charged ions and the dipole water molecules considerably modify the water structure. The small nickel ions with its high charge density will cause more disruption than the larger sulphate ion, but both become strongly associated with a sheath of water molecules (Fig. 12.1). The bonding between ion and solvation sheath confers a high degree of stability on the ions in aqueous solutions. The dipolar nature of the solvent, able to stabilise ions of either charge sign equally well, makes water an excellent ionic solvent. Ionic solvation destroys the ice-like component of the liquid with a result similar to that observed on melting, i.e. a decrease in volume as the 'space-wasting' ice structure is removed, and many strong electrolytes have a negative volume of mixing.

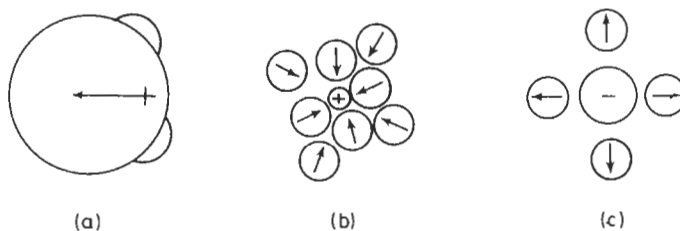
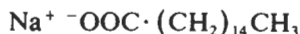


Fig. 12.1 (a) Water molecule, dipole structure, (b) solvation of a small cation, e.g. Ni^{2+} and (c) solvation of a larger anion, e.g. SO_4^{2-}

Aqueous solutions of non-electrolytes, especially of non-polar solutes, may show the reverse effect and increase the proportions of ice-like components. The non-polar part of organic electrolytes such as soaps and wetting agents may predominate in increasing the ice component. Thus solutes can be divided into two classes: *structure making* and *structure breaking*, and in some metal-finishing process solutions both types of solute may be added.

In certain cases it is impossible to satisfy both and there is a decrease in solubility of the least successful component. For example, a soap such as sodium palmitate, which in water is mainly



is very soluble, and the proportion of ice-like water increases to minimise interaction with the hydrophobic hydrocarbon chain. If sodium chloride is added to a concentrated soap solution, the ice-like structure is broken, and the increased concentration of 'free water' causes the palmitate to separate. Polar non-electrolytes like the lower alcohols have an even greater effect on the water structure than soaps. Being themselves capable of forming hydrogen bonds, they enter the 'iceberg' structure, increasing its stability. Methyl or ethyl alcohol added to solutions saturated with structure-breaking electrolytes, e.g. NiSO_4 in a plating bath, can withdraw water from the ionic solvation sheaths to form ice-like water, and now it is the electrolyte whose solubility falls. Soap, on the other hand, is more soluble in alcohol-water mixtures.

The ability of water to be oxidised or reduced at the plating-bath electrodes is in practice an important advantage, though it has a few drawbacks. The drawbacks are overemphasised in textbooks and the advantages ignored. An ion which is much more stable towards reduction than water is unaffected in the region of the cathode during electrolysis. With the margin of polarisation of 0.5–1.0 V, the manganous aquocation is the most stable which can be reduced in aqueous solutions, but because of the shortcomings of the metallic coating, manganese is not used, and the zinc aquocation is the most stable ion that can be reduced in large scale electroplating. A drawback is that the aquocations of aluminium, titanium, zirconium, niobium and tantalum are too stable. Their known corrosion resistance would make them important coatings but they cannot be electrodeposited. On the other hand there are numerous electrolytes whose presence is desirable in a plating bath but whose cations must not be reduced during electrolysis. The complete stability of cations like Na^+ , K^+ , NH_4^+ , Li^+ , Mg^{2+} , Ca^{2+} , Al^{3+} is then an advantage. Should the cathode be depressed (accidentally) below the normal working value, they are safe from reduction as hydrogen evolution acts as a 'safety valve' for excessive currents. The products of water reduction, hydrogen gas and OH^- ions are less likely to contaminate a large volume of valuable solution than are the reduction products of other materials.

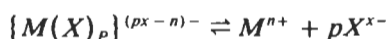
Similar considerations apply to oxidation. An anion which is considerably more stable than water will be unaffected in the neighbourhood of the anode. With a soluble anode, in principle, an anion only needs be more stable than the dissolution potential of the anode metal, but with an insoluble anode it must be stable at the potential for water oxidation (equation 12.4 or 12.5) plus any margin of polarisation. The metal salts, other than those of the metal being deposited, used for electroplating are chosen to combine solubility, cheapness and stability to anode oxidation *and* cathode reduction. The anions most widely used are SO_4^{2-} , Cl^- , F^- and complex fluorides BF_4^- , SiF_6^{2-} , Br^- , CN^- and complex cyanides. The nitrate ion is usually avoided because it is too easily reduced at the cathode. Sulphite,

which is used for gold plating, is nevertheless too readily oxidised at the anode, and provides an example of an ion used in one instance despite its drawbacks. The oxidation of water at the anode is also a reaction which does not contaminate the solution.

Much laboratory work has been performed to develop non-aqueous plating baths, using either organic solvents or ionic melts. In so far as the reduction of water is concerned, there are two rather different aims in view. Firstly, there is a search for solvents or melts sufficiently stable to allow electrodeposition of coatings of aluminium, titanium, etc. which are impossible with water. Secondly, there is a need for a non-aqueous solvent for metals such as cadmium, whose electrodeposition from water, while practicable and satisfactory, is always accompanied by hydrogen which can embrittle cathodes of certain high strength steels and other alloys (see Sections 8.4 and 13.3). Here the aim is to avoid hydrogen discharge. A practical drawback to the use of non-aqueous solvents is the accumulation of the by-products of solvent-electrode reactions leading eventually to the bath being poisoned.

Simple and Complex Ions⁴⁵

Amongst the common metals of the electroplating industry, only nickel is invariably reduced from its aquocation. Copper, silver, gold, cadmium and zinc are normally deposited from solutions of complex cyanides; tin, and chromium from oxyanions, and tin, in other cases, from a complex fluoride. Platinum-metal plating baths contain ions, all of which are complex; it is doubtful if any platinum-metal aquocation can exist in aqueous solution, such is the high tendency of these metals to form complexes. If a ligand, such as cyanide, can displace water from an aquocation to form a complex ion, the complex must be more stable, and the deposition potential is always more negative for a complex ion than for the equivalent simple ion. Let the equilibrium between aquocation M^{n+} , ligand X^{x-} and complex ion $\{M(X)_p\}^{(px-n)-}$ be



and

$$K = \frac{a_{M^{n+}} \times a_{X^{x-}}^p}{a_{\{M(X)_p\}^{(px-n)-}}}$$

where K is the *instability* constant for the complex ion, p is the *co-ordination* number. The potential below which deposition becomes possible is

$$E = E^0 + \frac{RT}{nF} \ln \left\{ \frac{K \times a_{\{M(X)_p\}^{(px-n)-}}}{a_{X^{x-}}^p} \right\}$$

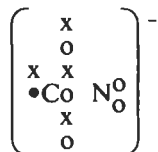
or

$$E = \left[E^0 + \frac{RT}{nF} \ln K \right] + \frac{RT}{nF} \ln \left\{ \frac{a_{\{M(X)_p\}^{(px-n)-}}}{a_{X^{x-}}^p} \right\} \quad (12.6)$$

where E^0 is the standard electrode potential for the simple ion/metal equilibrium. The two bracketed terms on the right of equation 12.6 constitute a

sort of ' E^0 ' for the complex ion, and as K is usually very small the second term is negative.

Complex ions used for electroplating are anions. The cathode tends to repel them, and their transport is entirely by diffusion. Conversely, the field near the cathode assists cation transport. Complex cyanides deserve some elaboration in view of their commercial importance. It is improbable that those used are covalent co-ordination compounds, and the covalent bond breaks too slowly to accommodate the speed of electrode reactions. The electronic structure of the cyanide ion is:

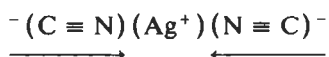


where electrons are contributed by the carbon atom (x), the nitrogen atom (o) and the cation (\bullet), e.g. Na^+ in the case of a sodium cyanide solution.

A soluble cyanide added to silver nitrate solution precipitates silver cyanide as an ionic compound:



The precipitate redissolves in excess soluble cyanide, and the complex ion is probably an ion-dipole co-ordination compound, i.e.



The solubility of $\text{Ag}(\text{CN})_2^-$ in water stems from the overall negative charge encouraging solvation with water dipoles, which uncharged AgCN does not. It is likely that the other cyanide complex ions of low co-ordination number have a similar structure.

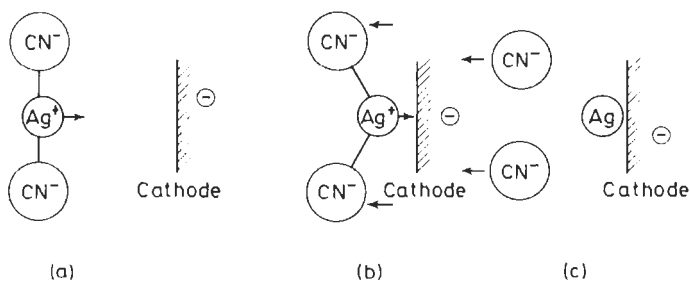


Fig. 12.2 Ion distortion by the field in the vicinity of a negative cathode. (a) Diffusion of anion to cathode, (b) diffusion and migration of distorted complex and (c) release of CN^- ions and incorporation of Ag into the lattice

When ions with this structure diffuse to the vicinity of a negative cathode, the ion is distorted by the field to become polarised, with the positive silver core nearest the cathode (see Fig. 12.2). Once within a critical distance the

field can assist transport of the distorted complex, discharge the silver core, and eventually repel the released cyanide anions. There are several practical advantages in plating from complex cyanides. The reduction in deposition potential is most important in the application of relatively noble metals to base substrates, while avoiding severe cathode corrosion. The important case of the copper cyanide bath is discussed later. The impeded diffusion of the complex anion, the energy needed to polarise and reduce the anion, and the diffusion 'barrier' produced by the high concentration of cyanide near the cathode, all contribute to a high overpotential for electro-deposition, which aids the production of even coatings on cathodes of uneven shape. The cyanide ions released after discharge of the metal from the complex modify the structure of the coating in a manner similar to that of addition agents, and it is probable that some cyanide is adsorbed. The result is that cyanide bath coatings are fine grained, hard, and may contain small amounts of carbon.

Some disadvantages stem from the same phenomena: impeded diffusion reduces the maximum practical rate of plating to well below that possible with aquocation baths. The cyanide ion is not entirely stable; both oxidation and reduction products accumulate, including carbonate. Carbonate is also formed in the alkaline cyanide baths (all cyanide baths are alkaline except some based on aurocyanides) by absorption of CO_2 from the air, and it is necessary either to replace or purify baths periodically. Much has been made of the toxicity of cyanides, but the other process solutions used in plating are generally extremely toxic and corrosive or caustic, and it is necessary to treat them all with respect.

Oxanions are important in chromium and tin plating. Although chromium plating baths have a simple formulation (chromium trioxide, sulphuric acid and water), hydrolysis and side reactions form a variety of polychromate ions. The cathode reactions are numerous and imperfectly elucidated; only about 5% of the charge passed produces chromium. As in cyanide baths the by-products behave as addition agents. The grain size of chromium electroplated under the normal conditions is the smallest encountered amongst metals. Tin coatings plated from stannate solutions are reduced from the $\text{Sn}(\text{OH})_6^{2-}$ ions, and are fine-grained.

The platinum-group metals are necessarily plated from complex solutions, since all platinum-metal salts form complex ions in water. The development of aqueous baths has hinged upon finding complex ions sufficiently *unstable* to be reduced; all the platinum group cyanides are far too stable. Because all the platinum metals are good catalysts for hydrogen evolution (high exchange current density) there is no useful margin of hydrogen overpotential over that predicted by equation 12.2. Nevertheless, aqueous plating baths have been devised for all the platinum group, although only palladium, rhodium and platinum find present commercial use.

The complex cyanides of transition metals, especially the iron group, are very stable in aqueous solution. Their high co-ordination numbers mean the metal core of the complex is effectively shielded, and the metal-cyanide bonds, which share electrons with unfilled inner orbitals of the metal, may have a much more covalent character. Single electron transfer to the ferri-cyanide ion as a whole is easy (reducing it to ferrocyanide, with no alteration of co-ordination), but further reduction does not occur.

Conducting Salts, Addition Agents and Other Ingredients of Plating Baths⁴⁶⁻⁴⁹

Plating baths contain a number of salts and compounds in addition to those of the ion to be reduced to metal. Much commercial electroplating is from 'proprietary' solutions whose use is covered by patents, and which are supplied completely or partly compounded. The precise composition is generally a trade secret, and the patents may sometimes be very widely drawn to include a larger range of compositions and ingredients than is successful. A broad classification of additional ingredients includes:

- (a) Those which maintain certain conditions but do not take part in electrode reactions; examples are electrolytes added to improve conductivity, pH buffer systems and ions which maintain complex ion equilibria.
- (b) Those which take part in the anode reaction, added to promote efficient dissolution of a soluble anode.
- (c) Those which take part in the cathode reaction by adsorption, co-deposition, or both, or by modifying the reaction; these ingredients alter the structure and properties of the coating and have an important bearing on its corrosion properties. The term *addition agents* is generally used for this class.

A particular ingredient often acts in more than one category.

Conducting salts are usually sodium, potassium or ammonium salts, or the acid of a stable ion already present from other ingredients. Apart from energy conservation, the higher the conductivity of a bath the better the distribution of thickness on complex shapes.

Addition agents are subdivided according to the main effect they have on the coating, i.e. grain refiners, brighteners (primary), brighteners (secondary), levellers, stress reducers and anti-pitting agents. Apart from the last, all these addition agents modify the growth process profoundly. They may be the ions of foreign metals which can co-deposit, or polar or ionic organic materials. They introduce irregular atoms or molecular fragments into the metal lattice or grain structure of the main metal of the coating, and alter the crystal structure. The macroscopic results are suggested by the names: smaller grain size, mirror-like surface, or a relatively smooth (level) surface on an initially rough substrate. These characteristics are not achieved without corresponding disadvantages. Foreign material from the addition agent is incorporated, up to 5% by weight for metallic co-deposition, less for organic agents. First- and second-order tensile stresses usually increase, hardness rises, ductility falls. First order tensile stress can exceed the tensile strength of the coating, but for some metals, particularly nickel, addition agents (stress reducers) are known which decrease first-order stress, though second-order stress is not reduced. The mechanical results are detrimental to corrosion protection, but the topographical results—fine grain, level and bright coatings, are favourable. The chemical results, on the evidence available, vary. The most extensively investigated case is nickel. Here it is almost universal practice to employ several addition agents together in a bright plating bath, one of which causes the incorporation of a small amount (about 0.02%) of sulphur, and reduces the corrosion resistance of bright nickel (see

Section 13.7). There are other systems (benzotriazole brighteners in copper, aldehyde-amine brighteners in tin) which enhance corrosion resistance.

Electroplating Anodes⁵⁰⁻⁵¹

The anode is usually soluble, and is made from a high purity form of the metal being deposited, or occasionally from an alloy. A soluble anode is often the cheapest and most convenient means of replacing the metal reduced at the cathode. Effective anode corrosion is important, and different examples present a variety of types of dissolution.

Copper anodes in the acid sulphate bath are an example of active anodic dissolution. They etch uniformly with low polarisation at 100% efficiency, forming little anode debris or sludge. Idle anode corrosion is very slow with dissolved oxygen reduction as the cathodic reaction. Copper anodes in the cyanide bath corrode easily providing there is sufficient excess or 'free' cyanide present. Polarisation is higher than in the acid bath, with a much lower maximum current density. At high current densities the rate of dissolution of copper exceeds the rate of supply of cyanide ions needed to form the cuprocyanide complex, and blue cupric aquocations form. Eventually the anode becomes passive and evolves oxygen. For special purposes where anode area is limited (e.g. in a Hull cell) an insoluble mild-steel anode avoids these troubles. A proportion of insoluble anodes or alternate use of soluble and insoluble ones is necessary, because anode efficiency exceeds cathode efficiency, and the metal content of the solution would rise continually if soluble anodes alone were used.

Nickel is normally plated from mixed solutions of nickel sulphate and chloride using soluble anodes. The standing potential of pure nickel anodes indicates they are passive in the idle bath, while in operation dissolution is by pitting corrosion brought about by chloride (Fig. 12.3). In all sulphate solutions, nickel anodes are passive and insoluble. Dissolution is aided by adding small amounts of sulphur or carbon to the nickel anode, which aid the breakdown of passivity ('depolarised anodes'). Nickel anodes produce a fine particulate 'anode sludge'; anode bags of finely woven cloth are used to retain much of this, and continuous filtration is needed to remove the rest, otherwise the corrosion resistance of the coating is severely degraded. Nickel can be used in the form of small 'chips' in baskets of titanium mesh. The titanium is passive and the surface is effectively insulated from electrolytic current exchange, but electrons released by the dissolving chips of nickel are able to pass via the metal-semiconductor contact with the basket to the outside circuit. Anode efficiency slightly exceeds cathode efficiency, but not sufficiently to increase the metal concentration, unless rigorous precautions are taken to return all the solution lost on surfaces removed from the bath.

Tin anodes dissolve by etching corrosion in acid baths based on stannous salts, but in the alkaline stannate bath they undergo transpassive dissolution via an oxide film. In the latter the OH^- ion is responsible for both film dissolution and for complexing the tin. Anodes must not be left idle because the film dissolves and thereafter corrosion produces the detrimental divalent stannite oxyanion. Anodes are introduced 'live' at the start of deposition, and transpassive corrosion is established by observing the colour of the film

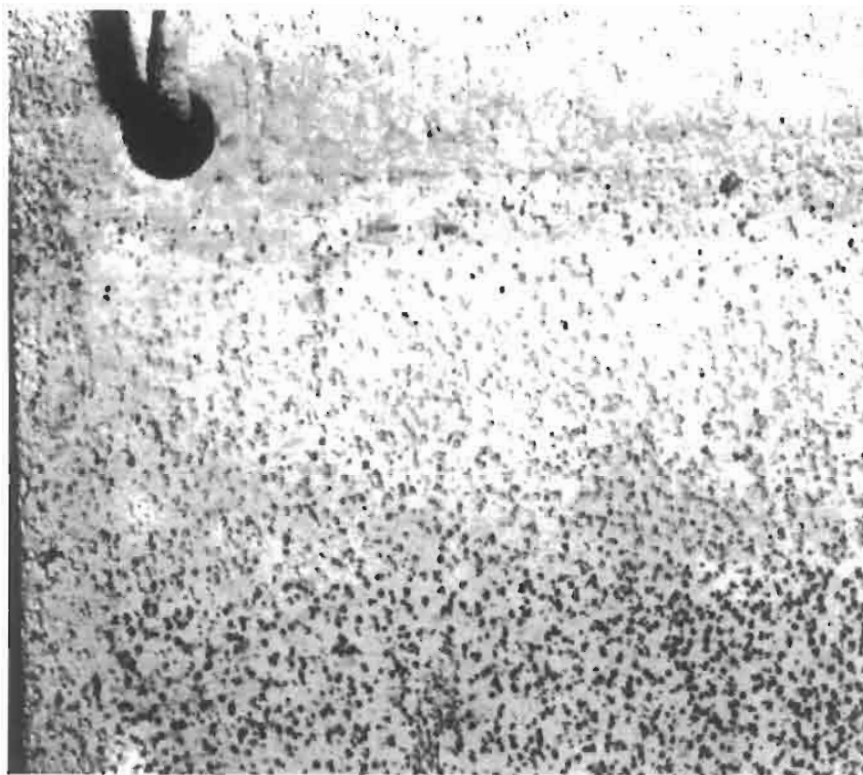


Fig. 12.3 Part of an anode from a nickel plating bath, showing dissolution by pitting corrosion

(pale yellow for correct operation) and the anode polarisation and by adjusting the immersed area. The anodes retain a smooth, quasi-polished surface, and no anode bags are needed. An alternative where anode filming is inconvenient is to use insoluble (passive) mild-steel anodes, and replace tin by adding a colloidal dispersion of stannic oxide.

Chromium plating from hexavalent baths is carried out with insoluble lead-lead peroxide anodes, since chromium anodes would be insoluble (passive). There are three main anode reactions: oxidation of water, reoxidation of Cr^{3+} ions (or more probably complex polychromate compounds) produced at the cathode and gradual thickening of the PbO_2 film. The anode current density must balance the reduction and reoxidation of trivalent chromium so that the concentration reaches a steady state. From time to time the PbO_2 film is removed as it increases electrical resistance.

Gold plating is another process where insoluble anodes are the rule. Soluble gold anodes would be technically satisfactory in some baths, but too tempting to thieves. A factor in their decline is the disappearance of gold coins, whose temporary sojourn in the anode circuit is alleged to have provided a form of corrosion beneficial to gold platers of earlier times. Insoluble stainless-steel anodes are now widely used, with graphite, platinised titanium and platinum mesh as alternatives. All suffer gradual deterioration. Stainless-steel anodes are pitted, especially in areas of high current density, and the

corrosion products may eventually give trouble. Platinised titanium sheds its platinum coating, becoming steadily more polarised. Platinum anodes used with cyanide solutions slowly corrode.

The potentials and corrosion data for some anodes in typical plating baths are listed in Table 12.1.

Table 12.1 Behaviour of anodes in plating baths

Plating bath	Anodes	Corrosion process		Current density (A/m ²)	Potential (V) (vs. S.H.E.)
		Idle	Working		
1. Watts' nickel NiSO ₄ ·7H ₂ O, 330 g/l NiCl ₂ ·6H ₂ O, 45 g/l H ₃ BO ₃ , 30 g/l pH 2·5 55°C	Nickel slab	Passive	Pitting	0 65 130 195	+0·08 +0·23 +0·27 +0·30
2. Bright nickel as (1) plus saccharin and 2-3 butyne 1-4 diol pH 2·2 50°C	Nickel slab	Passive	Pitting	0 390	+0·03 +0·36
3. Acid copper CuSO ₄ ·5H ₂ O, 150 g/l H ₂ SO ₄ , 50 g/l pH < 0 18°C	Pure copper	Slow etching	Uniform etching	0 130 260 390	+0·28 +0·32 +0·35 +0·38
4. Rochelle copper CuCN, 27 g/l NaCN, 38 g/l Na ₂ CO ₃ , 35 g/l KNaC ₄ H ₄ O ₆ ·4H ₂ O, 45 g/l pH 12·0 55°C	Pure copper	Slow etching	Uniform etching	0	-0·38
	Mild steel	Passive	Passive, evolving O ₂	0 130	+0·21 +1·09
5. Silver AgCN, 50 g/l KCN, 30 g/l K ₂ CO ₃ , 50 g/l pH 11·5 25°C	Fine silver	Slow etching	Uniform etching ↓ passive, evolving O ₂	0 32 ↓ 65	-0·24 -0·01 +6·0
6. Acid zinc ZnSO ₄ ·7H ₂ O, 250 g/l NH ₄ Cl, 15 g/l Al ₂ (SO ₄) ₃ ·18H ₂ O, 30 g/l Dextrose, 75 g/l pH 4·0 18°C	Zinc	Etching, rather rapid, H ₂ evolved	Uniform etching	0 163 325	-0·63 +0·30 +1·86
7. Chromium CrO ₃ , 400 g/l H ₂ SO ₄ , 4 g/l pH < 0 37°C	Pb/PbO ₂	Passive	Passive, evolving O ₂ , reoxidising Cr ³⁺ , etc.	0 1075	+1·5 +2·65

Corrosion of the Cathode⁵²⁻⁵⁷

At the start the cathode is invariably a metal different from that to be deposited. Frequently, the aim is to coat a base metal with a more noble one, but it may not be possible to do this in one step. When a metal is immersed in a plating bath it will corrode unless its potential is sufficiently low to suppress its ionisation. Fortunately, a low rate of corrosion is tolerable for a brief initial period. There are cases where even when a cathode is being plated at a high cathodic (nett) current density, the substrate continues to corrode rapidly because the *potential* (determined by the metal deposited) is too high. No satisfactory coating forms if the substrate dissolves at a high rate concurrently with electrodeposition. This problem can be overcome by one or more of the following procedures:

- (a) The use of a complex anion bath.
- (b) The use of a 'strike' bath.
- (c) The use of intermediate electrodeposits (undercoats or underplates).

The principles are illustrated by the following important commercial examples.

Zinc diecastings: complex baths and undercoats Diecastings are made from zinc with up to 8% aluminium, but from the viewpoint of corrosion they behave like zinc. Diecast parts are often plated with nickel and chromium for protection and decoration, but when zinc is immersed in a typical nickel plating solution it corrodes rapidly. There are two cathodic reactions: hydrogen is evolved and spongy nickel precipitates. If a diecasting is immersed 'live', corrosion and electrodeposition occur together as the potential for nickel deposition still leaves the cathode too positive to suppress zinc corrosion (Fig. 12.4). Standard practice is first to plate the zinc with an undercoat of copper, which is too noble to evolve hydrogen or reduce nickel ions. In the bath to which the data of Fig. 12.4 applied, the potential of copper was +0.042 V. Prolonged immersion led only to slow copper corrosion, with the reduction of dissolved oxygen as the cathodic reaction. This does not interfere with satisfactory nickel plating, and is entirely suppressed by live entry. The problem of applying a copper undercoat is solved by using the cuprocyanide complex bath. The acid cupric bath would present a worse problem than the nickel bath, with its lower pH and the greater oxidising power of the cupric ion. The stabilities of zinc and copper are reversed in alkaline cyanide, and zinc will not displace copper from cuprocyanide. Zinc immersed in the cuprocyanide bath can corrode to form either zincate or a complex zinc cyanide ion $\text{Zn}(\text{CN})_4^{2-}$, with two possible cathodic corrosion reactions, i.e. dissolved oxygen reduction or hydrogen evolution. However, high polarisation prevents either supporting rapid corrosion, and the situation is like that for copper in the nickel bath; a sound coating is possible and live entry suppresses corrosion. Once a coherent copper coating envelopes the zinc, the part is rinsed and transferred to the nickel bath.

The cuprocyanide plating bath is invaluable in numerous similar cases where a base substrate cannot be plated directly with the chosen coating. Steels, brass, bronze, beryllium copper and other substrates are copper

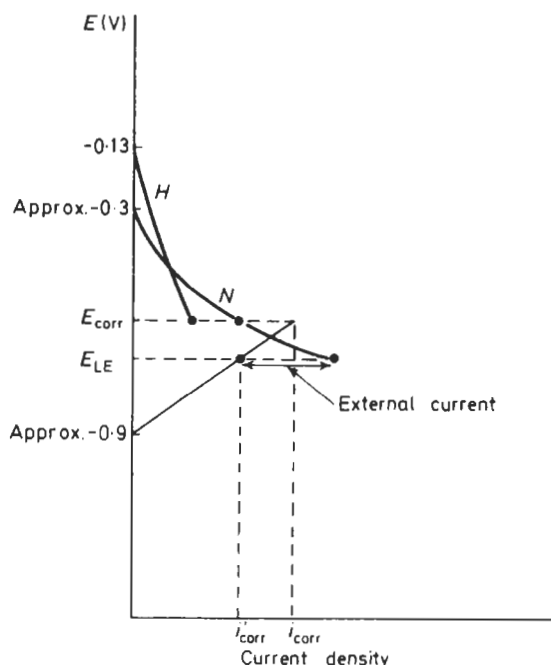


Fig. 12.4 Corrosion diagram for a zinc diecasting in a nickel plating bath, pH 2.2. There are two possible cathodic reactions, hydrogen evolution (H) and nickel ion reduction (N). The corrosion current i_{corr} is the sum of the partial cathode currents. Even with 'live entry' the potential E_{LE} is still too high to suppress corrosion, though the rate is reduced to i'_{corr}

underplated. Aluminium articles are ennobled, usually in two stages, i.e. first coated with zinc, which is in turn copper plated as described. Such is the utility of the cuprocyanide bath in circumventing cathode corrosion that although copper finds no significant use as a coating in its own right, cuprocyanide baths are found in almost every electroplating establishment.

Silver plating: 'strike' baths A 'strike' is usually a solution of special composition in which electroplating is initiated. After a short period of 10–150 s, the cathode is transferred to a normal bath. The term *strike* is also used when plating is initiated in the normal bath, but for 10–150 s under very different conditions (often much higher current density), continuing normally afterwards. Silver is electroplated from argentocyanide anions, i.e. $\text{Ag}(\text{CN})_2^-$. The bath is alkaline and contains 'free' CN^- . The argentocyanide ion is the least stable of the soluble complex cyanides, and therefore $\text{Ag}(\text{CN})_2^-$ is a strong oxidising agent towards other metals which form soluble cyanide complexes. Generally, the reaction



proceeds as written where M is a more base metal of valency n . Copper, gold, zinc, iron, etc. are all base metals by comparison, so a copper undercoat does not solve the problem. An immersion deposit of silver leads to blistering and loss of adhesion if electrodeposition is continued over it. The 'nobility gap' between copper and silver can be bridged by combining a shift

in the equilibrium of equation 12.7 with live entry. As a first step the cathode may be given a copper undercoat. The deposition potential for silver (special case of equation 12.7) is

$$E = \left(E^0 + \frac{RT}{F} \ln K_{\text{instab}} \right) + \frac{RT}{F} \ln \frac{a_{\text{Ag}}(\text{CN})_2^-}{a_{\text{CN}^-}^2} \quad (12.8)$$

where
$$K_{\text{instab}} = \frac{a_{\text{Ag}} + a_{\text{CN}^-}^2}{a_{\text{Ag}(\text{CN})_2^-}} = 1.8 \times 10^{-19}$$

At 298K, equation 12.8 is

$$E = -0.310 + 0.059 \log \frac{a_{\text{Ag}(\text{CN})_2^-}}{a_{\text{CN}^-}^2}, \quad (12.9)$$

and may be depressed by reducing the ratio in the last term, so a silver strike bath has a small concentration of metal and a large concentration of free cyanide. Equation 12.7 shows that a high concentration of free cyanide further decreases the nobility of the substrate, so some of the advantage is lost. One way of redressing the balance would be to have the substrate complex $M(\text{CN})_p^{(p-n)-}$ present in solution. Silver strike baths are formulated with cuprocyanide in solution, but curiously these are usually recommended for striking steel, while those recommended for copper alloys omit the cuprocyanide. The author uses the cuprocyanide silver strike for ferrous and copper alloys alike. The combination of low silver and high cyanide concentrations means the cathode potential at a relatively high current density is very low, and both charge transfer and diffusion polarisation are high. With live entry, the low potential suppresses substrate ionisation, and a detrimental immersion deposit of silver is avoided. A thin underplate—called a *flash*—is deposited from the strike, after which the normal bath is used. Dilute strike baths working at high current density cannot deposit thick coatings; continued electrolysis produces incoherent, powdery material. They have a low cathode efficiency and evolve considerable hydrogen.

Electroplating passive alloys Another application of strike baths reverses the case illustrated in the previous example. The strike is used to *promote* a small amount of cathode corrosion. When the passivation potential of a substrate lies below the cathode potential of a plating bath, deposition occurs onto the passive oxide film, and the coating is non-adherent. Stainless steel plated with nickel in normal baths retains its passive film and the coating is easily peeled off. A special strike bath is used with a low concentration of nickel and a high current density, so that diffusion polarisation (transport overpotential) depresses the potential into the active region. The bath has a much lower pH than normal. The low pH *raises* the substrate passivation potential E_{pass} , which theoretically follows a relation

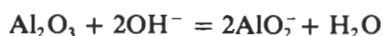
$$E_{\text{pass}} = E_{\text{pass}}^0 - 2.303 \frac{RT}{F} \text{pH} \quad (12.10)$$

When stainless steel is 'struck' the passive film is reduced and an adherent flash of nickel forms on the active metal surface. Deposition is continued in a normal bath.

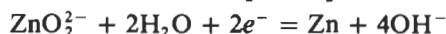
Table 12.2 Corrosion potentials of substrates of copper and steel, plated and unplated in same plating solutions. Deposition potential is accompanied by current density (A/m^2) in parentheses; the plated substrate's coating thickness was $2.5 \mu m$. The final column gives the potential below which hydrogen evolution is *possible*; only in the cuprocyanide is it observed

Plating bath	Copper	Steel	During plating	Plated copper	Plated steel	Hydrogen evolved below:
Watts nickel, pH 2.5, 55°C (not agitated)	+0.112	-0.238	-0.65 (130)	+0.132	-0.173	-0.148
Bright nickel, pH 2.2, 50°C (air agitated)	+0.042	-0.293	-1.22 (388)	-0.003	-0.138	-0.130
Cupric sulphate, pH < 0, 20°C	+0.275	approx. -0.35	-0.15 (388)	+0.265	—	> 0
Cuprocyanide, pH 12, 55°C	-0.378	-0.353	-1.21 (130)	-0.378	-0.388	-0.71
Argentocyanide, pH 11.5, 20°C	—	—	-0.58 (65) immersion deposit impedes measurement)	-0.24	—	-0.68
Zinc sulphate, pH 4.0, 20°C	+0.122	-0.578	-1.213 (162)	-0.64	-0.65	-0.24
18% w/v HCl pickle for ferrous metal, pH < 0	—	-0.17				> 0
3% w/v HCl pickle for copper alloys, pH 0	+0.17					0

Electroplating aluminium and its alloys requires a similar technique. In aqueous solutions it is impossible to lower the potential sufficiently to reduce an alumina film, so the substrate is immersed in a strongly alkaline solution capable of dissolving it:



The solution also contains a high concentration of zinc (as zincate), which is noble relative to aluminium. As metallic aluminium is exposed, it corrodes, reducing zincate ions and forming a coating of zinc:



The immersion deposit is necessarily somewhat defective, for the reasons already mentioned, though immersion deposits from complex ions are finer grained and more satisfactory than those reduced from aquocations. The zinc coating is, under the best conditions, an acceptable basis for a copper undercoat from the cuprocyanide bath, on which other coatings can be plated, but there is usually a fair proportion of rejects in commercial operation. Other processes similar in principle use tin or bronze immersion coatings.

Service corrosion effects Undercoats, 'flash' deposits produced by strike baths, and immersion deposits are potential sources of weakness. If their structure is faulty it affects the subsequent layers built on the faulty foundation. The greater the number of stages, the higher the probability of faults.

Additional metal layers can create bimetallic corrosion cells if discontinuities appear in service. The layer of copper beneath cadmium plate on aluminium (using a zincate plus cuprocyanide deposit technique) can cause corrosion troubles. When aluminium is plated with nickel and chromium, rapid service corrosion in the zinc layer causes exfoliation.

Corrosion potentials in plating baths The standing potentials of steel and copper (before application of current) are shown in Table 12.2, together with the standing potential of the plated metal and the potential below which hydrogen should, in theory, be evolved. The potential of the cathode during deposition at a typical current density is also given.

Factors influencing Structure⁵⁸⁻⁶⁴

Substrate effects: epitaxy and pseudomorphism Both the words *epitaxy* and *pseudomorphism* are derived from classical Greek, the former meaning literally *close to* or *close upon* an *arrangement, row* or *series* (technically an arrangement imposed upon a skin or layer, e.g. an electrodeposit, which is close upon a substrate) and the latter *false form* (technically a mineral or crystal displaying a form more characteristic of another material than its usual one). For many years the two terms were held to be synonyms for one phenomenon in electrodeposits. Since 1936 it has become clear that there are two related phenomena, on each of which one of the names is bestowed. Not all authors recognise this, nor is the usage employed here adopted uniformly. Both phenomena are of great practical importance.

Pseudomorphism received methodical study from about 1905. A micro-section taken across the interface between a substrate and an electrodeposit shows the grain boundaries of the former continue across the interface into the deposit (Fig. 12.5). As grain boundaries are internal faces of metal crystals, when they continue into the deposit the latter is displaying the form of the substrate. Hothersall's 1935 paper contains numerous excellent illustrations with substrates and deposits chosen from six different metals, crystallising in different lattice systems and with different equilibrium spacing. Grain boundary continuation and hence pseudomorphism is evident despite the differences.



Fig. 12.5 Pseudomorphism; grain boundaries in the substrate (S) are continued in the electrodeposit (D)

Epitaxy is a relation on the atomic scale between substrate and electrodeposit. Imagine that the interface of the micro-section were magnified about 10^7 times so that the rows of atoms in the metal lattice become visible. If the deposit shows epitaxy, there will be an ordered and regular relation between substrate and deposit atom positions (Fig. 12.6a). A non-epitaxial deposit shows no such relation (Fig. 12.6b). Direct experimental demonstration of epitaxy was first made in 1936 by Finch and Sun. Earlier, metallographers argued that pseudomorphism (which they could see) meant there must be epitaxy (which they could not), as grain boundaries are surfaces where the direction of lattice rows of atoms changes; if epitaxy were assumed to exist, pseudomorphism should result. Reversing the argument, pseudomorphism was taken as evidence for epitaxy (Fig. 12.6c).

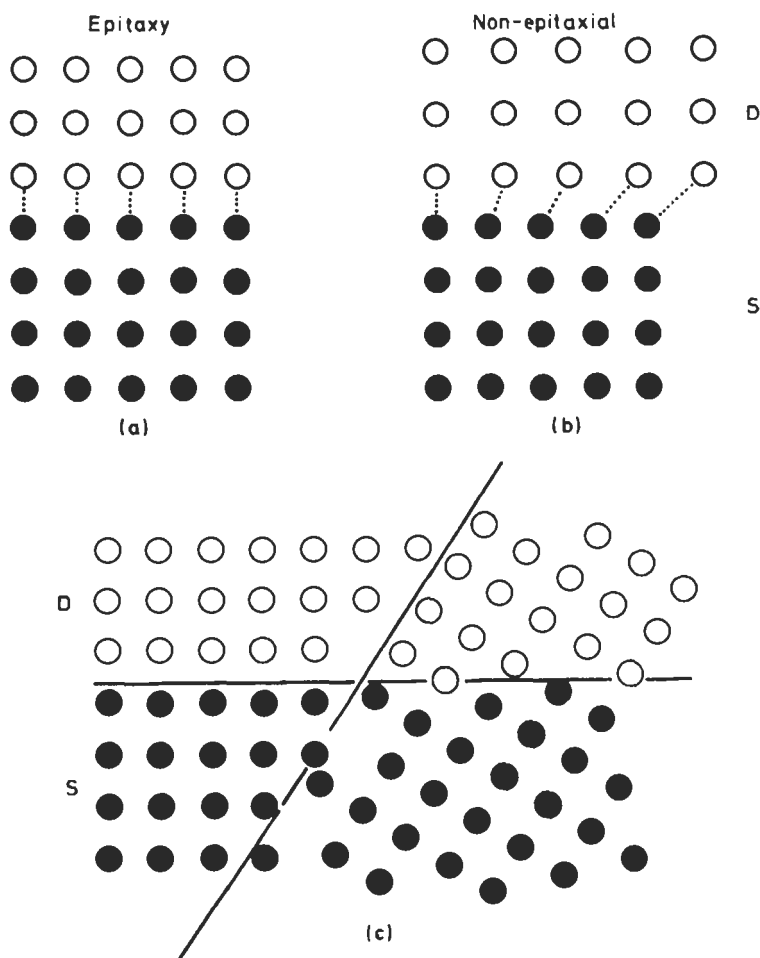


Fig. 12.6 (a) Co-ordination across a substrate *S*-electrodeposit *D* interface on the atomic scale produces epitaxy, (b) a non-epitaxial deposit has no co-ordination and (c) epitaxy would be expected to produce grain boundary continuation at the interface, though in fact grain boundaries often continue to thicknesses far greater than those at which epitaxy disappears

Electron diffraction investigations showed that epitaxy did indeed exist when one metal was electrodeposited on another, but that it persisted for only tens or hundreds of atomic layers beyond the interface. Thereafter the atomic structure (or lattice) of the deposit altered to one characteristic of the plating conditions. Epitaxy ceased before an electrodeposit is thick enough to see with an optical microscope, and at thicknesses well below those at which pseudomorphism is observed.

Epitaxy reflects the formation of metallic bonds between the dissimilar atoms at the interface. When the two metals crystallise in different systems, their relative orientation is that which promotes the maximum co-ordination and the maximum metallic bonding. The stability achieved by epitaxy overrides any lost due to the lattice strains imposed. These strains may be considerable; 'stresses' calculated from the bulk elastic moduli are correspondingly high, and sometimes puzzle the uninitiated if they exceed the bulk tensile strength. It is an oversimplification to regard the interface as being highly stressed; were the 'stress' which seems to be parallel to the interface reduced by some means to zero, the energy that would have to be put into the bonds normal to the interface would be much greater than that released. The simple concept of stress in a homogeneous alloy is not applicable to the peculiar case of a substrate-electrodeposit interface. The latter is unique in having metallic bonds carried across a very sharp boundary.

The practical result of epitaxy is a very high degree of adhesion between coating and substrate. The force needed to separate the interface is similar to that needed to break the metals on either side. Where a true metallic bond forms at an epitaxial interface it is only possible to measure adhesion if the bond is the weakest of the three near the interface. An adhesion test based on breaking the joint indicates only which of the three is weakest. For practical purposes any epitaxial joint will have a strength more than adequate for service conditions.

Non-epitaxial electrodeposition occurs when the substrate is a semiconductor. The metallic deposit cannot form strong bonds with the substrate lattice, and the stability conferred by co-ordination across the interface would be much less than that lost by straining the lattices. The case is the converse of the metal-metal interface; the stable arrangement is that in which each lattice maintains its equilibrium spacing, and there is consequently no epitaxy. The bonding between the metallic lattice of the electrodeposit and the ionic or covalent lattice of the substrate arises only from secondary or van der Waals' forces. The force of adhesion is not more than a tenth of that to a metal substrate, and may be much less.

Epitaxial growth is prevented if semiconducting films of grease, oxide, sulphide, etc. cover the cathode surface. These occur when pretreatment is inadequate, when plating baths are contaminated, or when, as with stainless steel, aluminium, titanium, etc. an oxide film reforms immediately after rinsing. Low adhesion resulting from non-epitaxial electrodeposition is used in electroforming to promote easy separation of deposit and substrate. When semiconductors or non-conductors are to be electroplated, a form of dovetail mechanical joint (achieved as outlined above) is essential. Means similar to those for stainless steel and aluminium have been devised to deal with other alloys which passivate readily. Sometimes, even with special methods, some oxide remains so that the electroplated coating is anchored

only by small epitaxial areas. There is risk of failure. Thermal stress or relatively mild abrasion may part the interface and cause the unanchored areas to blister. Adhesion is improved by post-plating annealing. The oxide at the interface is dissolved in one or other metal, or diffuses to grain boundaries, etc. and alloying at the interface produces the desired metallic bond.

Pseudomorphism has less desirable consequences, and usually means are sought to suppress it. If the substrate has been scratched, ground or abrasively polished, or if it has been cold rolled or cold formed, the surface is left in a peculiar state. Cold working reduces the surface grain size, and produces deformed, shattered and partly reoriented metal. It may produce microcrevices between the deformed grains, and, with some processes, non-metallic impurities and oxides are embedded in the surface. The disturbed state of the substrate is copied by a pseudomorphic electrodeposit with several consequences (Fig. 12.7). One is aesthetic; it has often been noted that almost invisible abrasion of the substrate develops as more prominent

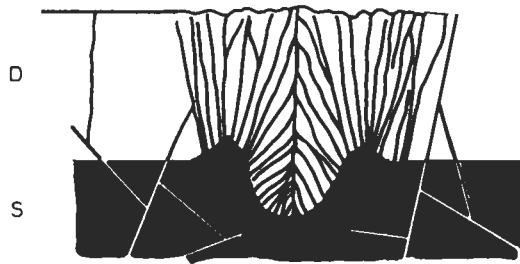


Fig. 12.7 The disturbed structure of a scratch, with fragmented and distorted grains, is perpetuated by a strongly pseudomorphic electrodeposit

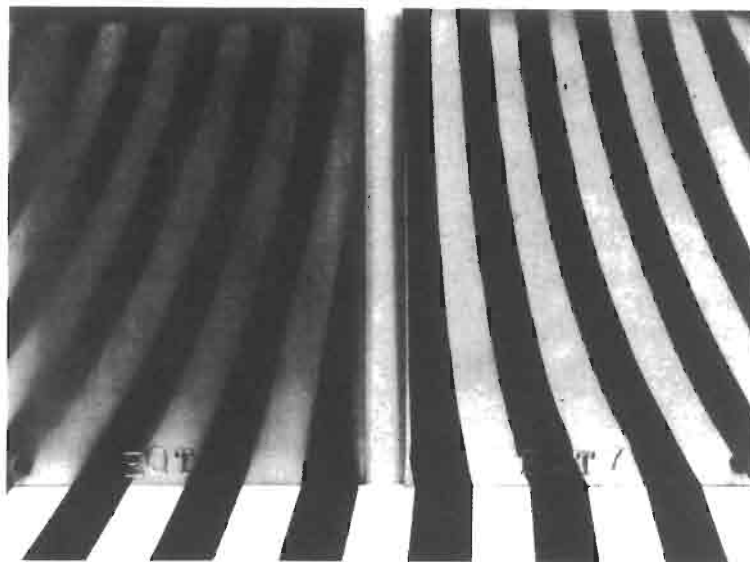


Fig. 12.8 A fairly strongly pseudomorphic bright tin deposit (left) has its brightness impaired by the shattered surface layer produced on steel by cold rolling. When this layer is removed, the deposit is mirror bright (right). Coating $5\text{ }\mu\text{m}$ thick

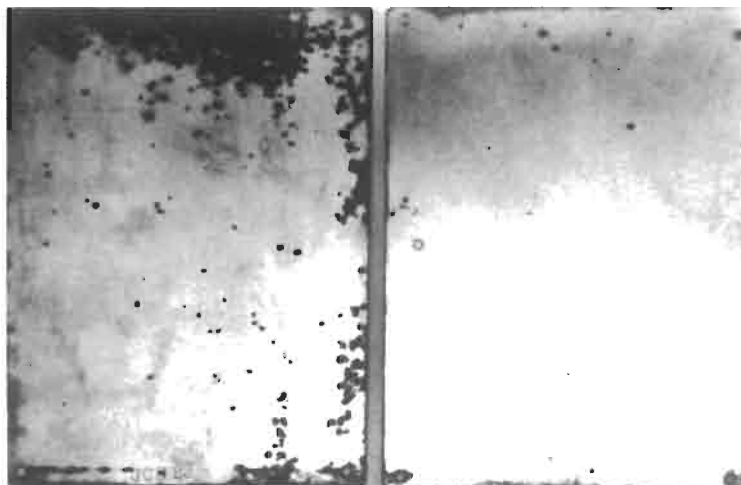


Fig. 12.9 Corrosion resistance of tin-nickel electrodeposit impaired by pseudomorphic porosity originating on cold-rolled steel surface (left). Panel on right has had the shattered grain surface removed by chemical polishing ($0.125\text{ }\mu\text{m}$ removed). Coating thickness $15\text{ }\mu\text{m}$; panels exposed 6 months to marine atmospheric corrosion (Hayling Island)

markings in the deposit. A chalk mark on steel produces local abrasion, hardly noticeable when the chalk is wiped away. If a strongly pseudomorphic electrodeposit is applied the chalk mark reappears indelibly on its surface. A bright deposit may have its lustre greatly reduced by pseudomorphic growth on a deformed surface (Fig. 12.8). The corrosion protection is reduced if pseudomorphism with a deformed substrate leads to discontinuities at ill-fitting deposit grains (Fig. 12.9). A pseudomorphic coating usually presents a dull or rough crystalline appearance. When the crystal form of the substrate is copied in the deposit, growth generates faces of simple index. An artificial face of high index soon grows out when plated. Tradition demands a featureless mirror surface on metal coatings, and a way of producing this which has attracted much commercial effort is by using brightening addition agents. Micro-sections of electrodeposits from the more effective bright plating baths do not exhibit pseudomorphism. The deposit usually shows no grain structure, but instead a series of light and dark bands parallel to the substrate (Fig. 12.10). Pseudomorphism is suppressed by the addition agent adsorbing on and blocking areas taking part in pseudomorphic growth. In the initial stages of bright plating the addition agents adsorb at similar points on the substrate. Growth commences from fewer substrate nuclei when annealed nickel is plated in a bright nickel bath than in a dull (Watts) bath without additions. In the earliest stages of deposition, replicas of the surface show evidence of pseudomorphism even in bright baths (the substrate grain boundaries are carried into the deposit) but this is suppressed rapidly as the thickness increases. The aim with bright plating baths is to inhibit growth sufficiently to suppress pseudomorphism, but not so much as to suppress epitaxy and adhesion. An excessive concentration of addition agent will also suppress epitaxy, so that deposition occurs on to an adsorbed layer of brightener. Brightener adsorption is often potential dependent and trouble may occur first at high current density (low potential) areas.

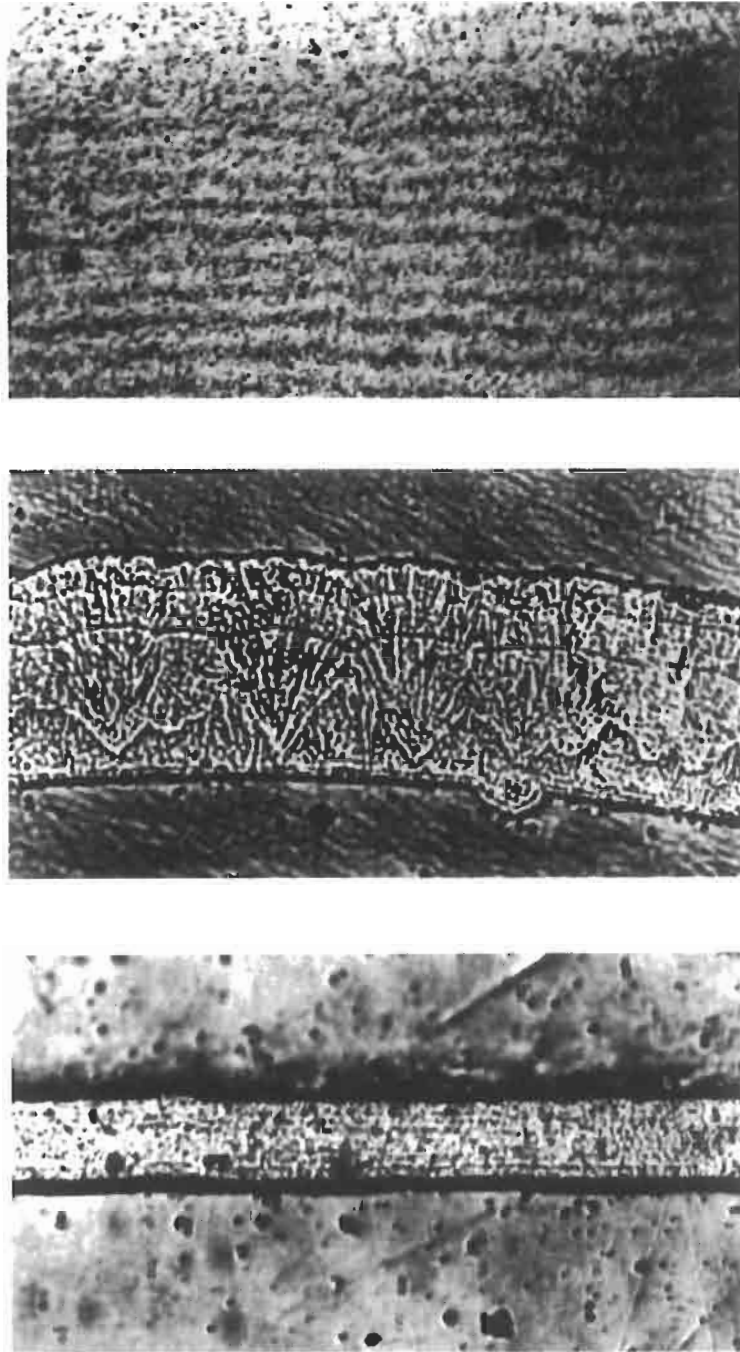


Fig. 12.10 Banding often observed in micro-sections of bright electrodeposits. (a) Bright tin (courtesy of the Tin Research Institute), and (b) and (c) Bright gold

Electrolyte effects⁶⁵⁻⁶⁹ As a deposit becomes thicker, the influence of the substrate diminishes, and eventually the structure is characteristic only of the electrolyte composition, the temperature, current density and mode of agitation. A great variety of structure is observed; some are analogous to those seen in cast metals, but others are obtained only by electrodeposition. Crystalline deposits from baths containing little or no addition agent often develop a preferred orientation texture. Some bright deposits show a texture, but in general as growth processes are progressively inhibited by increasing addition agent concentration or by using more active materials, the deposit becomes progressively finer grained and loses preferred orientation textures.

The compositions of baths chosen for practical use result in initial rates of lateral growth much greater than the rate of outward growth. This is a desirable feature; it causes the coating to become continuous at low thicknesses. The opposite condition of a faster rate of outward growth is undesirable, and results in a non-coherent deposit. Predominantly outward growth occurs when the transport of metal ions becomes slow compared with their rate of discharge, i.e. it is favoured by high current density, low temperature and lack of agitation. Lateral growth processes are then starved of material to support them, but outward growth moves the deposit towards the supply, and the prominences formed benefit from greater diffusive flux. There are strong pressures in industrial production to increase electroplating rates, which carry a danger of using high current density and causing a shift to outward growth. In baths where the coating is electroplated from aquocations at high cathode efficiency, the onset of lateral growth is fairly sharp. Cathodes have a range of local current density, and the coating on the high current density areas becomes friable, dark coloured and rough as the transition is reached. Such coatings are termed *burnt* and the corrosion protection is degraded. With baths working in the acid pH range there is the complication that once an appreciable part of the current is used to reduce water, the pH at the cathode rises and insoluble hydroxides are precipitated and incorporated in the coating. With complex cyanide baths the onset of 'burning' is less sharp. There is normally considerable simultaneous hydrogen discharge, and as the current density rises there is no sharp limiting current density for metal discharge. Addition agents raise the lateral-outward transition to higher current densities, by inhibiting outward growth. Nevertheless all electroplated coatings show signs of deteriorating properties if the baths in which they are produced are worked at sufficiently high current density.

Form of current passed through cell⁷⁰⁻⁷⁹ Commercial electroplating began with pure d.c. from galvanic cells. Later, for many years d.c. generators were used. Their current output is unidirectional but with a superimposed ripple. Part of the ripple stems from the angular motion of the armature coils during the period they supply current to a commutator segment, and part from variations of contact resistance at the commutator. Generators have been superseded by transformers and rectifiers. Copper-oxide, mercury-arc, selenium, germanium and silicon rectifiers have been used, and examples of each are to be found in service. These devices supply varying unidirectional current whose form depends on the number of phases in the input and the circuit used. A half-wave single-phase rectifier provides a pulsating current; a full-wave three-phase set has a much smoother output.

Alternating currents with asymmetric forms have been used, mainly for electroforming and thick engineering deposits. Where the cycles are slow, e.g. several seconds, the term *periodic reverse current* (p-r-c) is used. The benefit claimed for p-r-c plating is that smoother, thick deposits result from selective dissolution of peaks in the reverse part of the cycle. This assumes the electrode process reverses during the anodic period, which is not always the case. In chromium plating the coating becomes passive in anodic periods, while in acid gold baths based on aurocyanide, the process is also irreversible. More recently, asymmetric a.c. with a much higher frequency of 500 Hz was found to alter beneficially the properties of nickel from chloride baths.

Pulses of unidirectional current have been used to modify coating properties. When plating starts it is possible, for a time, to use a current much higher than the steady state limit, drawing on the stock of ions near the cathode. Provided sufficient time is allowed between pulses, a coating can be built of layers plated at much higher current density than normal. Improved gold coatings were produced by relatively rapid pulses. The technique of *barrel plating* results in pulse plating of an irregular sort, with pulse durations of the order of a second and inactive periods rather longer.

Chromium plating from chromic acid baths is more sensitive to the source of current than most other processes, sufficiently so for commercial operators to use at least three-phase rectifiers as a rule, and to take precautions against any temporary break of current during voltage regulation. A recent investigation showed that the ripple introduced by thyristor control of rectifiers was detrimental to chromium electrodeposits.

Industrial Electroplating Techniques⁸⁰⁻⁸²

Electroplating is usually a finishing technique applied after an article has been completely fabricated. Fairly large articles, from cutlery to motorcar bumpers, are dealt with by vat plating. They are suspended by a conducting connection in a rectangular tank or vat of electrolyte. The anodes are arranged about the periphery of the tank. For small runs the cathodes may be suspended by copper wire wrapped round a suitable part, but for longer runs a plating jig is used. This is a copper frame with phosphor bronze spring contacts to hold the work, and insulated, usually with a p.v.c. coating, on all but the contact points. The point of contact between wire or jig and the article becomes a weak part in the coating, and some thought should be given to providing or selecting contact points in insignificant areas.

Vat plating is used sometimes with articles too large for complete immersion. Printing, calendering, drying and similar rolls are part-immersed and revolved continuously during plating. However, it is much more difficult to plate half an object, reverse it, and complete the other half later; the 'join' between the two deposits is rarely satisfactory.

Small objects, nuts, bolts, screws and small electrical parts are plated in a revolving barrel. Electrical connection is made by a conductor immersed in the tumbling mass, and electrodeposition, which is confined to the outer layer of the mass at any instant, takes place in intermittent stages for any individual object. The coating is abraded during the process. The peculiarities of chromium deposition set it apart, and the normal barrel-plating

processes are not used. In so-called *chromium* barrels the small parts travel and tumble along a helix inside a rotating cylinder during deposition, and are electroplated for a much greater proportion of the time than are parts in normal barrels.

Brush plating is a special technique which dispenses with a container and uses a swab soaked in electrolyte applied to the work. In *jet* plating a stream of electrolyte is applied to the cathode. Both are methods of *selective* plating, applying an electrodeposit to only a part of an article. Little has been published about the techniques or the properties of coatings they produce.

Continuous plating of wire and strip is, unlike the preceding techniques, a prefabrication process. The production of tinplate is the largest scale continuous operation, but any electrodeposit may be applied this way. Subsequent fabrication processes are likely to damage the coating, so that pre-coating is best reserved for ductile coatings which are anodic to the substrate in service, as is the case for tin.

*Rinsing*⁸³⁻⁹²

Between all stages of immersion (cleaning, pickling, plating, post-plating treatment) work has to be rinsed. Once the hydrophobic solid has been removed, metal surfaces withdrawn from solutions carry a film of liquid. The solution lost this way is known as *drag-out*. A film 10 μm thick is the minimum retained by smooth, well-drained, vertical surfaces. On rough or horizontal surfaces and in recesses it is much thicker, as it is also with viscous solutions. During rinsing the film is diluted, and the ratio of the final concentration to that present initially is the *dilution* ratio. The dilute material is carried forward to the next process, and clearly the highest concentration of impurity permissible before the subsequent process is affected adversely determines the maximum dilution ratio which can be allowed. Sometimes there is a minimum dilution ratio; between nickel plating and chromium plating it is essential that the rinsed metal surface does not become passive, and prolonged rinsing carries a danger of eliminating the slight but important amount of rinse water corrosion which keeps the surface active between stages.

Usually rinsing troubles are caused by a dilution ratio that is too high. If incoming work passes through a process stage, and the drag-out from that stage is in turn discarded in a subsequent rinse, the maximum concentration of material carried into the bath is equal to that in the film carried over. However, there is an increasing tendency to conserve materials and steps are taken to return drag-out losses. In so doing the impurities are also returned, so conservation measures require a reduction in the dilution ratio of the preceding rinse. Inadequate intermediate rinses are detrimental to the corrosion resistance of the coating because carried-over impurities impair the functioning of plating baths. Inadequate final rinsing leads to increased corrosion of the coating, and to staining. Staining, which is a serious aesthetic problem with decorative coatings, may itself arise from corrosion. Some stains are caused by the precipitation of dissolved solids when rinse water evaporates, but in other cases they are caused by corrosion supported by the presence of an electrolyte in the rinse water.

Post-Plating Treatments⁹³⁻⁹⁶

Where the corrosion resistance of a coating depends upon its passivity, it is common to follow plating with a conversion coating process to strengthen the passive film. Zinc, cadmium and tin in particular are treated with chromate solutions which thicken their protective oxides and also incorporate in it complex chromates (see Section 15.3). There are many proprietary processes, especially for zinc and cadmium. Simple immersion processes are used for all three coatings, while electrolytic passivation is used on tinplate lines. Chromate immersion processes are known to benefit copper, brass and silver electrodeposits, and electrolytic chromate treatments improve the performance of nickel and chromium coatings, but they are not used to the extent common for the three first named.

The tin coatings as deposited in tinplate manufacture are not bright. Until comparatively recently bright tin electrodeposition was not practised commercially, there being no reliable addition agents. To produce bright tin on tinplate and other products, the process of *flow melting* or *flow brightening* is used; tinplate is heated by induction or resistance, and plated articles by immersion in hot oil to melt the tin, which flows under surface tension to develop a bright surface. While the tin is molten it reacts to form an alloy layer with the substrate. The alloy layer alters the corrosion behaviour.

Other electroplated articles are heated after plating to expel hydrogen which has entered the substrate during cleaning, pickling and plating, and which embrittles some metals, mainly high-strength steels. Generally speaking alteration of the deposit structure and properties is not desired. Another use of post-plating heat treatment is to improve adhesion, as already mentioned (p. 12:26).

Mechanical polishing, formerly the principal means of producing bright coatings, has become less important with the extension of the use of brightening addition agents. Mechanical polishing reduces the thickness of a coating, and may cut through to the substrate. As corrosion resistance is related to thickness, mechanical polishing can be detrimental. It may also increase porosity.

Properties of Electrodeposits**Thickness**⁹⁷

Coating thickness is one of the most important quantities connected with corrosion resistance, and its measurement and control is a feature common to all electroplating operations and in all quality specifications. In some cases coating thickness has functional importance, e.g. where there are fitting tolerances, as with screw threads. In most cases however it is the connection with corrosion resistance that makes thickness important. Where the coating is anodic to an area of substrate exposed at a discontinuity the coating is slowly consumed by corrosion, but the criterion of failure is the appearance of substrate corrosion product. This does not form until almost all the coating is consumed. Coatings which are cathodic to the substrate must have no discontinuities if substrate corrosion is to be suppressed.

The criterion of failure is usually the same. Freedom from discontinuity is also related to thickness. Discontinuities have three origins: spontaneous cracking to relieve internal stress, pores formed during the growth of the coating (see p. 12:41), and abrasion and wear. The last two causes, i.e. porosity and wear, both exhibit diminishing incidences as thickness rises. Apart from the peculiar case of electrodeposited chromium, internal stress cracking is a sign of incorrect plating conditions. Broadly speaking, thickness and corrosion resistance increase together. The thickness of an electroplated coating is never uniform. On the *significant* area (i.e. that on which corrosion resistance and other special properties are important) of a plated surface there are two important thicknesses, i.e. (a) *average thickness*, which determines the production rate and plating costs; and (b) *minimum local thickness*, which, as the weakest link in the chain, determines the corrosion resistance. The ideal is to make these equal; the larger the difference the greater the waste of metal. The difference can be reduced by special procedures, but at a cost.

When the cathode is being plated, the electrical field is not uniform. Both electrodes are equipotential surfaces, so that prominent parts of the cathode, e.g. corners, edges, protuberances, etc. which are relatively nearer the anode are plated at a higher average current density, resulting in a thicker coating. Recesses and more distant parts are more thinly plated. The distribution of thickness tends to be the reverse of that found with paints, hot-dipped and other coatings which are applied as liquids. Liquid-applied coatings are thin on sharp edges, and thick in recesses because of the effects of surface tension and radii of curvature.

The numerous factors which contribute to the thickness distribution can be divided into two groups, i.e. (a) those connected with the nature of the plating bath (see below) and (b) those to do with the geometry of current paths in the bath, including the shapes of the electrodes.

Throwing Power⁹⁸⁻¹⁰⁵

In a given plating cell, thickness distribution is found to vary with bath composition, current density, temperature and agitation. It is common to speak of the *throwing power* of a plating bath. The throwing power of chromic acid baths is *poor*, i.e. there is a relatively large difference between maximum and minimum local thickness; conversely, the throwing power of alkaline stannate baths is *good*, i.e. there is much less difference in the local thicknesses. Strictly speaking the bath composition should be qualified by the conditions of use, as they affect throwing power. Otherwise, the usual conditions are implied. A numerical *throwing index* can be calculated from the performance of a plating bath in a cell of standard geometry. Two widely used cells are (a) the Haring-Blum cell and (b) the Hull cell (Fig. 12.11). The Haring-Blum cell was devised for throwing index measurement; the Hull cell is used mainly to study the effects of varying bath composition.

The Haring-Blum cathode is divided into two equal plane areas, distant ℓ_1 and ℓ_2 from a common anode, and a quantity called the *primary current density ratio* P is defined as

$$P = \ell_2 / \ell_1$$

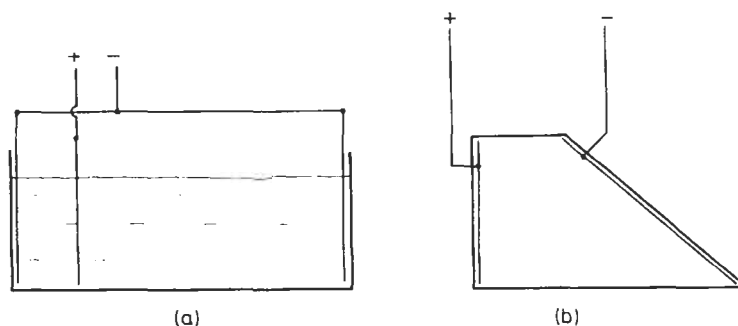


Fig. 12.11 (a) Haring-Blum cell for throwing index measurement, in elevation and (b) Hull cell (plan view) which can also be used for measuring throwing indices

This is the ratio in which the current would divide, if electrolytic resistance were to control its flow entirely. The metal distribution ratio M is the ratio of the thicknesses of the coating actually deposited during a measurement. There are several numerical scales of throwing index T , but Field's is widely adopted:

$$T = 100 \frac{P - M}{P + M - 2} \% \quad (12.11)$$

On this scale, zero represents the case when $M = P$, and electrolyte resistance is the main factor. Throwing power can be worse, down to a limit $T = -100\%$ when $M = \infty$, i.e. no deposit at all on the far cathode. Conversely, when $M < P$, T is positive. Were M to reach 1.0 despite the difference in position, $T = +100\%$. At one time $+100\%$ was regarded as an unrealisable limit, but conditions have been found for which $T = +150\%$ in a Haring-Blum cell.

The Hull cell cathode has a continuous variation of current density along its length, and there are equations which give the primary current density at any point not too near the end. If the local thickness is measured at two points for which P is known, T can be calculated. The real current distribution is a function of cathode and anode polarisation as well as of the resistance of the electrolyte. The metal distribution ratio will be

$$M = \frac{(V - \Delta E_1) \ell_2 \epsilon_1}{(V - \Delta E_2) \ell_1 \epsilon_2} \quad (12.12)$$

where V = cell potential difference between anode and cathode,
 ΔE = total potential difference caused by polarisation (anode and cathode) on the cathode area indicated by the subscript and
 ϵ = cathode efficiency as indicated by the subscript.

As ΔE will be a function of current density, T will be a function of electrode area, and comparisons should therefore be made with cells of standard size. Equation 12.12 shows that high throwing indices will result when polarisation rises steeply with current ($\Delta E_1 \gg \Delta E_2$) and cathode efficiency falls steeply ($\epsilon_2 \gg \epsilon_1$). The primary current ratio, $P = \ell_2/\ell_1$, affects the result because

by altering the currents the polarisation terms are altered. For example, with an acid copper bath in a Haring-Blum cell, 194 A/m² average c.d.:

$$\begin{array}{cccc} P = & 2 & 5 & 11 & 23 \\ T\% = & +7 & +11 & +22 & +41 \end{array}$$

An increase in conductivity usually increases T because it increases the proportion of polarisation in the total cell potential difference and lowers the ratio $(V - \Delta E_1)/(V - \Delta E_2)$. Changing the conductivity of an acid copper bath with sulphuric acid produced the following result (291 A/m² average c.d., $P = 5$):

$$\begin{array}{cccc} \text{Conductivity (S/cm)} & 0.08 & 0.15 & 0.26 & 0.30 \\ T(\%) & +5 & +11 & +13 & +27 \end{array}$$

where S is the SI unit of conductance (siemens).

Many baths in which metal is reduced from complex anions (e.g. cyanide baths, stannate baths) give high throwing indices because both polarisation and cathode efficiency variation favour a low value of M . The cathode efficiency for a typical copper cyanide bath (40°C) was:

$$\begin{array}{cccccc} \text{Current density (A/m}^2\text{)} & 32 & 65 & 129 & 258 & 388 \\ \text{Cathode efficiency} & 76 & 68 & 56 & 34 & 21 \end{array}$$

The throwing index for the cyanide bath is usually about +40% and rises as the cell current is increased to as high as +85%. Aquocation baths give values near $T = 0$, though conditions may be selected which give much higher figures if there is a steeply rising section of the polarisation curve. Chromium plating baths invariably have large negative throwing indices, despite deposition from a complex ion. The cause is the anomalous *rising* trend of cathode efficiency with current density and the existence of a minimum current density *below* which the efficiency is zero. A typical bath (400 g/l CrO₃, 4 g/l H₂SO₄, 38°C) gave:

$$\begin{array}{cccccccc} \text{Cathode current density (A/m}^2\text{)} & 199 & 253 & 384 & 763 & 1785 & 5130 & 30800 \\ \text{Cathode efficiency (\%)} & 0 & 5.9 & 11.9 & 13.9 & 18.8 & 22.7 & 24.4 \end{array}$$

If the current density on the far cathode in a Haring-Blum cell was 199 A/m² or less, $T = -100\%$.

Throwing indices measured in a Hull cell differ from those in a Haring-Blum cell because of the differences in geometry. In a Hull cell several pairs of points can be found which have the same primary current ratio, but for which M and hence T are found to vary because of polarisation changes.

Current Path Geometry¹⁰⁶⁻¹¹⁰

The polarisation and cathode efficiency terms in equation 12.12 cannot be altered in practice to improve thickness distribution, as they tend to be decided by overriding considerations. It is usual to accept the distribution obtained without special precautions as being the best commercial solution, although the average thickness needed to achieve the necessary minimum

local thickness may be high. Where this approach does not serve there are a number of methods of altering the term ℓ_2/ℓ_1 in equation 12.12:

- (a) By using shaped (conforming) anodes, additional (auxiliary) anodes or 'bipolar' anodes to bring anode areas nearer to cathode recesses. Insoluble anodes are better where they are applicable as, once made, they do not alter shape during use.
- (b) By using non-conducting shields of plastic or glass to equalise the current path lengths.
- (c) By placing auxiliary cathodes ('robbers' or 'thieves') near high-current-density points to divert deposition. This does not save metal, but has the merit that auxiliary cathodes can be incorporated into jigs for long runs in automatic plating machines. Auxiliary cathodes are used in heavy chromium deposition where metal waste is secondary to the cost of removing excess chromium when grinding to precise dimensions. Where a number of small parts are plated together on a jig, it is usually possible to dispose them so that they serve as 'robbers' for each other.
- (d) By attention to certain 'rules' when designing articles which will be finished by electroplating. Many external contours are chosen for reasons of style. It helps to avoid features like sharp recesses, which are bound to cause trouble. A simple rule is the '1 in ball test' or perhaps the '25 mm ball test': if there is any part of a surface which a ball of this diameter cannot touch when rolled over it, there will be difficulties. There are other design aspects, covered in specialist publications, attention to which improves the corrosion resistance which can be imparted by plating (see also Section 11.4).

Structure-dependent Properties¹¹¹⁻¹¹⁶

Composition of the electrodeposit Attention has been drawn to the dependence of structure on both substrate and plating conditions, and the transition in properties which occurs across the section of a deposit. Most commercial electrodeposits have a high purity, yet in a sense impurities are vital to their successful application. Alloy electrodeposition possesses a literature whose bulk attests the subject's fascination for research (which the author shares), but is out of proportion to the extremely limited commercial applications. Alloys in general metallurgical practice provide a variety of mechanical properties; in electroplating the range of properties desired is narrower, and it can generally be achieved by altering the structure of a single metal deposit through changes in the plating bath composition or plating conditions. The microstructure of an electrodeposit can be altered much more than that of a cast and worked metal. This is because the deposit forms well below its melting point, where crystallisation processes are hindered by the virtual absence of solid-state diffusion. Consequently, very small amounts of 'impurity' absorbed at important growth sites on the surface cause large changes in the structure of what is, chemically, almost pure metal. The structure is metastable, but permanent as long as the electrodeposit is not heated. A variety of mechanical and physical properties are a

reflection of the structure: hardness, ductility, tensile strength, internal stress, electrical and thermal conductivity, etc. As the structure of an electrodeposited metal is altered by changing the plating conditions, the mechanical and physical properties also alter. A plot of structure-dependent properties against the plating variable usually shows the various properties moving in parallel or inverse motion, and over ranges not accessible in cast and worked metal of the same composition. However, if electrodeposits are heated to temperatures where moderate mobility of the atoms is possible, their properties rapidly revert to 'normal'. The corrosion resistance of electrodeposits depends much more on chemical composition rather than on structure, so that the corrosion resistance of a particular metal is retained for a wide range of mechanical and physical properties.

The 'impurities' responsible for modifying the structure may originate from: water (dispersed oxides); adsorbing ions, especially cyanides; organic addition agents parts of which are incorporated; or ions of a second metal which are co-deposited. Some regard deposits in which the impurity is a small amount of a second metal as an alloy, but generally they have the same sort of metastable structures as are obtained with non-metallic impurities, rather than those of stable alloys of the same composition. The 'alloying' metal serves to cause and perpetuate a non-equilibrium structure whose real basis is the low temperature of the electrocrystallisation process. Generally, the corrosion properties of the various different structures of a given metal are much the same, with the notable exception of nickel containing sulphur from addition agents, which has already been mentioned.

Internal Stress¹¹⁷⁻¹²⁰

Electrodeposits are usually in a state of internal stress. Two types of stress are recognised. First order, or macro-stress, is manifest when the deposit as a whole would, when released from the substrate, either contract (tensile stress) or expand (compressive stress) (Fig. 12.12). Second order or micro-stress, occurs when individual grains or localities in the metal are stressed, but the signs and directions of the micro-stresses cancel on the larger scale. The effects of first order stress are easily observed by a variety of techniques.

Second-order stress is difficult to observe and much less extensively studied. The causes of internal stress are still a matter for investigation. There are broad generalisations, e.g. 'frozen-in excess surface energy' and 'a combination of edge dislocations of similar orientation', and more detailed mechanisms advanced to explain specific examples.

Tensile first-order stress is a corrosion hazard in coatings cathodic to the substrate. Compressive stress is not usually troublesome, nor is stress of either sign in anodic coatings. Less can be said about high second-order stress, though it may well cause brittleness. If tensile stress is large enough, the coating cracks and a cathodic coating will fail to protect, as illustrated in Fig. 12.13. Tensile stress below the level needed for spontaneous cracking lowers the fatigue limit of a substrate. Tensile stress can in several cases be reduced to safe values by fairly minor changes in microstructure and plating conditions, insufficient to upset other desirable properties. Saccharin is an addition agent for reducing stress in nickel; additions of ammonium chloride



Fig. 12.12 An electrodeposit showing unusually high compressive stress. A 150×150 mm copper sheet was insulated with lacquer on one side and electroplated with Sn-35 Ni alloy. The high compressive stress has caused the sheet, originally flat, to coil in the manner shown, with the electrodeposit *outside*

reduce stress in tin-nickel alloy, and small changes in bath temperature and $\text{CrO}_3 : \text{H}_2\text{SO}_4$ ratio reduce stress in chromium.

The effects of tensile stress in the various layers of nickel plus chromium coatings are complex, and internal stress in both chromium and nickel (post-nickel strike or PNS) layers can be harnessed to produce beneficial cracking ('microcracking').

Ductility, Hardness, Wear, Strength¹²¹⁻¹²⁴

The mechanical properties reflect very closely the structures of electrodeposits. The softest, most ductile, weakest form of a particular metal is that with a large crystal size, deposited with minimum polarisation from baths which have no addition agents. This is the type of deposit in which pseudomorphism is strongest. In terms of the accepted deposition mechanism, there is the least inhibition of anion mobility as the deposit grows, and least inhibition of those sites at which equilibrium growth would occur. This electrodeposit has properties the nearest to those for the annealed metal, but even so tends to be somewhat harder. Because of pseudomorphism the properties near the substrate interface may be greatly modified if the latter has a metastable structure, especially one with very small grains produced by mechanical working. The deposit in turn becomes 'work hardened' by pseudomorphic growth.

When electrodeposition is inhibited the metal becomes harder, less ductile and increases in tensile strength. Metals deposited from acidic solutions of

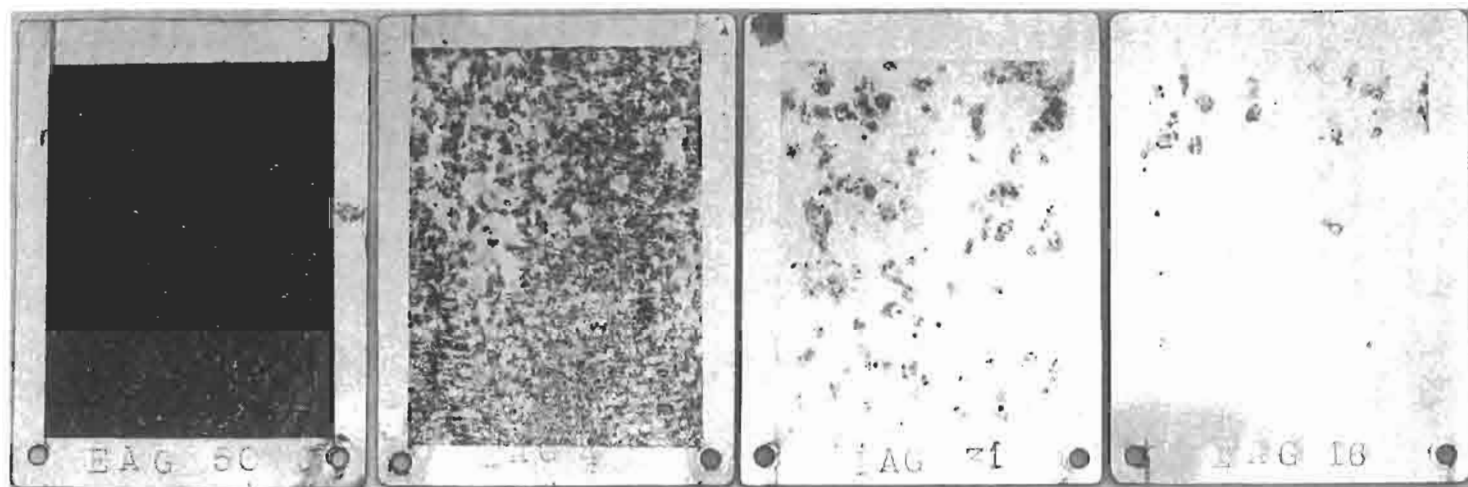


Fig. 12.13 Cracking in a cathodic coating due to tensile stress which exceeds the coating's strength, leading to loss of protection. All $5\text{ }\mu\text{m}$ coatings of tin-nickel on steel with internal stresses. From left to right: EAG 50, 134 N/mm^2 tensile; EAG 4, 86 N/mm^2 tensile; EAG 31, 57 N/mm^2 tensile; EAG 16, 127 N/mm^2 compressive

aquocations become harder when the pH is raised to near the value at which the hydroxide precipitates. Co-deposited oxide acts as an addition agent, giving small grained, hard deposits. Hard nickel is produced for engineering surfacing from high pH baths. Many metals can be electrodeposited in extremely hard forms from inhibited baths, but they tend to become brittle, with high internal stress, so that the true tensile strength is hard to establish. Ductility necessarily falls as hardness rises, and coatings become more susceptible to damage by impact, reducing their protective value if they are cathodic to the substrate. Some applications of electroplating depend on the production of unusually hard and wear-resistant forms of corrosion-resistant metals. Thick coatings of chromium and nickel are applied to numerous steel parts to combine wear resistance with corrosion resistance. Thick or engineering chromium electrodeposits crack repeatedly during deposition, but the cracks are subsequently sealed and none should traverse the entire coating. Thick chromium coatings have practically no ductility, and because of their defective structure they have a low effective strength. They serve best on stiff substrates.

Gold coatings on separable electric contacts and slip rings make use of the high hardness possible with electrodeposition to resist wear. Rhodium is another metal which can be exceptionally hard. Thick coatings have a cracked-sealed structure similar to that of chromium.

Interdiffusion with the Substrate¹²⁵⁻¹²⁶

A thin metal coating on a metal substrate is not a stable entity; greater stability would be attained if the coating were to diffuse evenly throughout the substrate. Fortunately, at ambient temperatures most of the usual combinations interdiffuse so slowly as to present no practical problem. At high temperatures however, many coatings diffuse quickly. Diffusion in a few systems at moderate temperatures causes corrosion problems. Difficulties can occur with tin, which, with its low melting point of 231°C, is relatively 'hot' at room temperature. On copper and copper-alloy substrates diffusion transforms the tin into the intermetallic phases Cu_6Sn_5 and Cu_3Sn . At 100°C the transformation is accelerated, and 5 μm of tin may become wholly alloyed within a year. The alloy coating may pass as tin having a silvery colour, but it is much harder and has a very stable passivity. One use of tin on copper is to facilitate easy joining by soldering, but the alloy has a high melting point and is not easily wet by solder. Thin 'tin' coatings on copper which have become wholly alloyed in storage are difficult to solder. Sometimes extremely thin coatings (0.25 μm) used purely for solderability become wholly alloyed in a few weeks. Parts should not be stored too long, and very thin coatings are a false economy (Section 9.5).

Tin will protect copper from corrosion by neutral water. Pure tin is anodic to copper, and protects discontinuities by sacrificial corrosion. Both intermetallic phases are strongly cathodic to copper, and corrosion is stimulated at gaps in wholly alloyed coatings. An adequate thickness of tin is needed for long service, e.g. 25–50 μm . Another diffusion problem occurs with tin-plated brass. Zinc passes very quickly to the tin surface, where under conditions of damp storage zinc corrosion products produce a film

which greatly impairs solderability. An underplate of copper, or better still nickel, usually cures this trouble.

A similar problem, i.e. diffusion of the substrate through the coating to corrode at the surface, arises with gold-plated copper. Many gold coatings are used to ensure a low electric contact in electrical connectors. Gold is pre-eminent because of the absence of stable-corrosion-product films under most service conditions, but it is expensive, so coatings are kept as thin as possible. Electronic devices may operate at fairly high temperatures (100–150°C), and significant amounts of copper may diffuse through the coating to produce a film of oxide on the surface, nullifying the contact value of the gold. Nickel underplate mitigates this trouble (though increasing plating difficulties). To reduce costs, attempts have been made to dilute gold with cheaper metals, while retaining gold-like corrosion properties. Cadmium has been used as a diluent, but while quite high cadmium-golds are gold-like at 25°C, at higher temperatures cadmium oxidises at the surface. Pure gold is preferred for high-temperature contacts.

Porosity¹²⁷⁻¹³⁹

In the very earliest stages of electroplating the substrate carries discontinuous areas of deposit growing around nuclei. Lateral growth causes the great majority of growing edges to coalesce with sufficient perfection to be impervious to corrosive gases and liquids. On normal metallic substrates a few edges do not grow together, and a gap remains in the coating. As the coating thickens the gap is propagated as a channel through the coating, to form a *pore*. Under the conditions chosen for practical electroplating, pores diminish in cross section as deposition continues, and pore density (pores per unit area) falls as thickness increases. The corrosion which occurs when pores allow liquid and gaseous corrosive agents to reach the substrate varies in importance according to the relation between the corrosion potentials of deposit and substrate, the corrosive environment and the function of the coating.

If the environment favours wet corrosion processes, relative polarity is the main consideration. If the coating is anodic, porosity is seldom of any serious consequence. The cathode is the very small area of substrate exposed at the base of the pore, and the restricted channel limits the diffusion of reactants and products. The large anode area provided by the coating reduces the bimetallic corrosion current density thereon. Two important examples of this type are zinc coatings on steel in cold waters or the atmosphere and tin coatings on steel on the inside (but not the outside) of a sealed, air-free can of wet food. In the first case oxygen is the cathodic reactant; in the second it is hydrogen ions (or water). Where the coating is cathodic, porosity enables the exposed substrate to corrode. In most cases this is detrimental; the exception is found in some multi-layer nickel plus chromium coatings where certain forms of porosity in the chromium layer are harnessed to divert the direction of corrosion to the overall benefit of coating life. In other cases corrosion at pores causes trouble. In wet atmospheric corrosion, substrate corrosion product, if coloured and insoluble, spoils decorative appearance. In immersed conditions or condensing atmospheres,

if the corrosion product is soluble intense pore corrosion will perforate sheet metals. Here a porous coating may accelerate corrosion when compared with the uncoated substrate.

Porosity causes little trouble when corrosion is restricted to dry processes (oxidation). Corrosion products block the pores and stifle the reaction.

There was much research into the causes of porosity in nickel deposits when it was thought to be the main cause of failure in nickel and chromium plate. Much was discounted as it became clear that nickel pitting at discontinuities in the chromium was the factor determining service life. Porosity remains relevant to the corrosion resistance of simpler cathodic coatings, and especially for gold. The use of gold for contact surfacing since about 1950 has revived the importance of studies of porosity. Pores in gold coatings allow films of substrate corrosion product to contaminate the surface and to destroy the low contact resistance of the gold. Sulphides, which are one of the products of corrosion by service atmospheres, have a particularly high rate of spreading over gold in the solid state (Fig. 12.14).

Pores originate on substrate areas known as *precursors*, which are of at least three types. Firstly, an obvious cause is an inclusion of foreign material which is a semiconductor or insulator—particles of oxide, sulphide, slag, polishing abrasive, etc. When electrodeposition starts, inclusions will not be nucleation sites, and they will impede the lateral growth and coalescence of crystals from neighbouring nuclei. Secondly, substrates whose surface grain structure has been severely disturbed by cold working (abrasion, cold rolling, drawing, etc.) have precursors whose physical state (rather than chemical difference as in the first type) precludes coalescence of the electrodeposit. This is probably an effect of pseudomorphic growth. Relatively low-temperature annealing (as low as 210°C for steel) greatly reduces the effect, and further cold work increases it again (Fig. 12.15). The third type of precursor

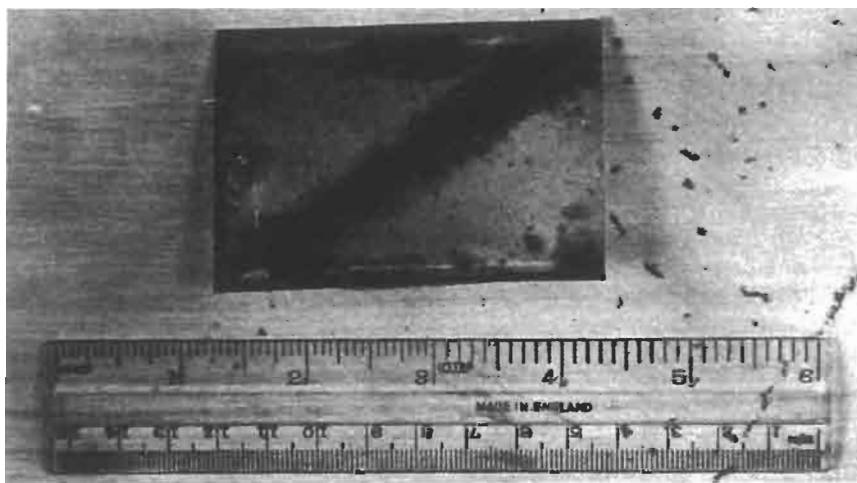


Fig. 12.14 Spread of silver sulphide from discontinuities in gold electrodeposits on silver substrates. The gold was deliberately scratched and the specimen exposed for 24 h to an atmosphere containing 10% SO_2 . Immediately after this the sulphide stain extended 0.2 mm. Five years later, the stain extends to about 13 mm, after storage in a normal indoors atmosphere

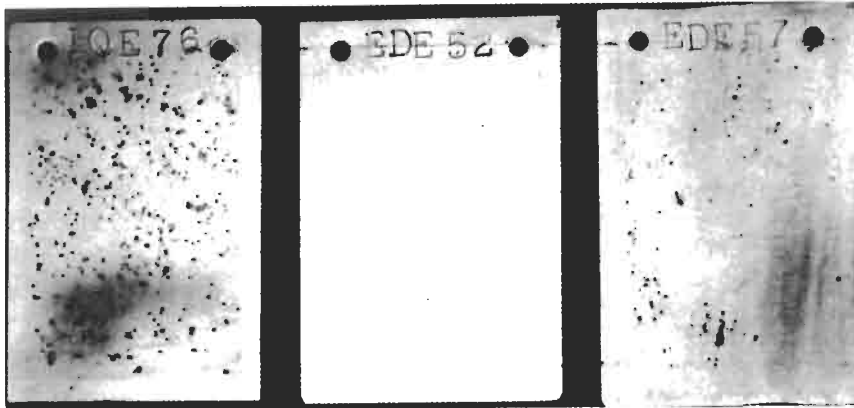


Fig. 12.15 Porosity caused by a cold-worked substrate. Left (EQE 76) cold-rolled steel as received; centre (EDE 52) steel bright-annealed in vacuum before plating, 2·5 h at 700°C; right, annealed steel, further cold-rolled (0·914 mm to 0·864 mm) produces porosity again. No steel was removed from the surface; 5 μ m tin-nickel electrodeposit

is a crevice in the substrate. If the depth is great relative to the width, the electric field is excluded and deposition does not occur within the crevice. Lateral growth is impeded once the edges from neighbouring nuclei reach it in much the same way as with a non-conducting inclusion. A pore caused by any type of precursor in one electrodeposit becomes in turn a precursor for a second deposit plated over it. There may be other forms of precursor.

In a particular area of substrate there will be a number of precursors, distributed over a range of sizes, and reflecting the nature, composition and

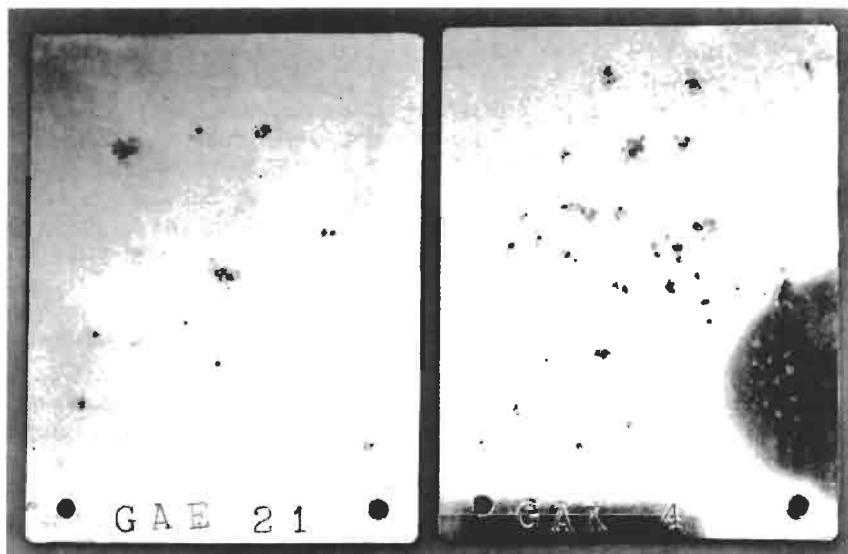


Fig. 12.16 Increase in porosity of an electrodeposit caused by mechanical polishing. Left, 7·5 μ m unpolished coating; right, polished with lime finishing compound. The average thickness removed by abrasion was 0·1 μ m

history of the metal. In principle anything affecting the substrate surface will affect porosity in an electroplated coating.

As deposition continues growth gradually diminishes the surface opening of a pore, and if continued to a sufficient thickness, closes it, leaving a sealed cavity filled with solution. Small precursors will generate pores which seal relatively early, large ones will require greater thicknesses. The total pore density revealed by a test which renders pore sites visible falls as thickness increases. The minimum thickness required to seal a precursor of fixed size will depend on the rate of narrowing of the surface opening, and, as a growth process this will reflect the plating conditions. Because of this, the density of pores still open at a fixed thickness is a function of all the plating conditions, i.e. of the composition of the plating bath, of temperature, current density, agitation and anything affecting deposit growth.

Post-plating treatments affect pore density, either by closing pores which are still open or opening sealed ones. It has been asserted that mechanical polishing in general, or flow-melting for tin, are both processes which could seal pores and reduce porosity. It is also conceivable that polishing might cut-open sealed pores, and likewise under flow-melting conditions the vapourisation of solution trapped in sealed pores could disrupt the coating and recreate discontinuities. The author has come across no convincing demonstration of porosity reduction by either treatment, but has found experimental evidence for porosity increases (Fig. 12.16).

Recent Developments

Although the basic principles of electroplating remain unchanged, the extent of development and variety of application have widened substantially¹⁴⁰. In this section some notable developments will be cited.

The development of new solutions and processes continues unabated, driven as ever by commercial and proprietorial needs as well as pressure from pollution and effluent control demands and simply for the need to supersede some less-than-satisfactory solutions. Non-cyanide solutions are continually being sought for metals such as gold, copper, cadmium and zinc, but cyanide remains pre-eminent as the most effective and best understood complexant available and few competitors have been discovered. The other ecological *bête-noire* is hexavalent chromium, and several commercial bodies offer non-toxic trivalent chromium plating solutions, both aqueous and organic based although only the former is believed to be industrially viable. The solutions are based upon chromic sulphate or chloride salts, a complexant such as hypophosphite, glycollate, thiocyanate etc. and a depolarising anode reactant which could include ammonium ions or a separated anode compartment. The cathode efficiency is still below 50% and only thin coatings can be reproducibly produced (10 μm max.), but pollution difficulties are largely eliminated. This has proved to be a difficult area, but the number of successes is expected to increase¹⁴¹⁻¹⁴⁴.

A separate problem is the establishment of a good process for electroplating aluminium which must necessarily be based upon a non-aqueous electrolyte. This field is a history of many discoveries, but few developed processes have been claimed, although recent work suggests that at least

two good possibilities exist which may make inroads in the electronics field rather than in the other important area of wide steel strip aluminising¹⁴⁵⁻¹⁴⁶.

In his classic treatise, Brenner² reported that over 500 alloy electro-deposition systems had then been studied in depth—that number has now been substantially increased—yet barely 10 to 20 have any real degree of industrial exploitation. The list continues to grow and the present type of work on alloys can be divided into three classes:

1. The development of new alloys in new fields; for example the development of molybdenum and tungsten with iron, cobalt or nickel for coating of dies and nozzles, or the development of palladium-nickel alloy as an alternative to gold for connectors.
2. The development of new alloys as a means of modifying existing electrodeposits; for example the production of hard gold by alloy co-deposition of copper, cadmium etc. to yield 23 or 18 carat alloys, or the use of zinc alloys for improved electrogalvanised coatings.
3. The development of new solutions for established alloys; for example the replacement of fluoborate for lead-zinc brasses.

With industry proving to be so conservative about binary alloys it is hardly surprising that ternary alloys receive little attention. Nevertheless, two ternary alloys at least have become commercially available: iron-chromium-nickel (so-called stainless steel) for both functional and domestic markets and an electronic connector and solderable alloy based on copper-zinc-tin.

The field of composite materials has been the major growth area of materials engineering in the last twenty years, based mainly on ceramic and polymer materials. While electroplated (and electroless) composites show more modest growth this is attributable to the necessary limitation of metal matrices. Thus the principle is to take a well-established metal deposition process (gold, cobalt, copper, nickel, tin) and to induce co-deposition of second-phase particles, thereby enhancing coating properties such as hardness, wear and oxidation resistance. The key to successful co-deposition is having particles of appropriate size and density, typically 0.1–10 μm size, suitably suspended in solution by a non-swirling agitation technique, co-deposition occurring by physical entrapment or electrophoretic attraction. Such particles include oxides (e.g. Al_2O_3 , TiO_2 , ZrO_2 etc.) or refractory hard compounds (e.g. Cr_7C_3 , WC, Mo_2C etc.), abrasives such as diamond, lubricants such as MoS_2 or graphite and low-friction material such as p.t.f.e. A substantial literature exists, relating to both process and product characteristics and reference should be made to two notable reviews^{147,148}. Several obvious applications have to a large extent been achieved; e.g. second-phase hardening by Al_2O_3 of gold without serious loss of electrical conductivity, high-temperature erosion or wear resistance of nickel or nickel-cobalt gas turbine or jet engine alloys improved by using carbide incorporation, and improved surface lubricating of nickel by incorporation of p.t.f.e. particles.

The use of current or voltage pulsing during electroplating has long been known to have a beneficial effect on the deposition process rate and on the deposit itself in terms of grain size variation, internal stress, levelling etc. Periodic reverse techniques (cycle time of 10–10² s) are widely employed in electrowinning and electrorefining operations while pulse plating (cycle time

of 10^{-3} to 1 s), which requires more sophisticated electronics, is now of considerable interest for metal finishing. The basic theory has been discussed by Ibl¹⁴⁹ who has defined the parameters involved. Claims for improved brightening, levelling and throwing power are of especial interest in electronics, but are not yet fully substantiated in many instances¹⁵¹.

The cooperation of industrial and engineering designers with the metal finishers, who are frequently required to perform the near-impossible as a consequence of poor communication, is notoriously bad largely as a consequence of the nature of sub-contract industrial relationships. To meet this need an important new standard—BS 4479—has been issued; although it is ostensibly a revision of the old standard it is in reality a new standard written essentially as a code of practice. Invaluable advice is given to finishers and designers alike: the challenge now is to have it widely read and appreciated!

Increasing awareness of the cost-effectiveness of electroplating processes has led to critical appraisals being made of cell design, not only to improve the product through improved efficiency and economics of the process itself, typically through the costs of electricity. Thus the use of more conductive solutions, combined with minimisation of the anode-cathode spacing can yield a 40% saving in electrical power. However, not all of this saving is necessarily desirable if chemical costs thereby increase and the peripheral cost of solution heating has also to be increased. Similarly, improved agitation and filtration may also be considered for optimisation studies. This 'chemical engineering' approach has found increasing value¹⁵²⁻¹⁵⁶, not least in the development of new types of plating cell specifically for metal recovery from trade effluent, dragouts and rinses¹⁵⁷⁻¹⁵⁹. In fact the number of new designs far outnumbers the number of optimising and independent assessment studies so that it is not possible to name a 'best-buy', and time is needed for commercial realities to eventually declare a winner, albeit not on entirely objective terms.

The largest-scale electroplating activities have always been carried out by the steel industry in an atmosphere largely divorced from traditional metal finishing. Upwards of 20% of all steel produced may be coated, the products of relevance to this chapter being tinplate, its alternative for packaging 'tin-free steel' and zinc electrogalvanised steel in the form of sheet, strip and wire. During the last twenty years little advance has been made in the electroplating stage of tinplate production, the electrolytes and additives have changed little and the plant design remains essentially the same—marked changes have occurred in other aspects of tinplate production, however. The alternative 'tin-free steel' or TFS, has settled into a well-established sector of the market, largely for lacquered beer and beverage cans and non-critical container applications such as oil, polish, some paint etc. Its invention is attributed to Japan in the period 1958–1965 and it has been widely exploited. The technology is based on that of tinplate as a fast cathodic process (1–20 s) in a chromic acid-based solutions yielding a coating ($<0.1 \mu\text{m}$) consisting of chromium metal and chromium oxide, Cr_2O_3 ¹⁶⁰⁻¹⁶¹. Its virtue is cost-effectiveness for every specific application, and as such it has replaced tinplate for 10–40% of the market, depending upon the country concerned.

By contrast the zinc coating product area is seeing rapid developments after a relatively static period when hot-dipped and electrogalvanised

products occupied well-defined niches for thick (20–150 μm) and thin (5–20 μm) coatings, respectively. The driving force can be found in the automotive industry which is looking towards car bodies having 5–10 year warranties for which paint and phosphating treatments on steel sheet are inadequate. Two separate types of coated product are emerging. Firstly, electrogalvanising combined with a modified TFS process giving a highly passivated zinc coating: this is probably the cheapest and easiest option¹⁶². Secondly, alloyed zinc electrogalvanising to give improved sacrificial corrosion performance whilst remaining relatively thin (< 15 μm), a requirement imposed by the body-forming processes. To this end the zinc alloys favoured are those with nickel, iron, manganese or tin at 0.5–10% levels¹⁶³. It is too early to predict which alloy will dominate the field.

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12.2 Principles of Applying Coatings by Hot Dipping

General

Dipping of metals into molten lower melting point metals is the oldest, simplest and generally the cheapest method of forming a surface coating. The basis metal must withstand the temperature without undesirable changes in properties. To obtain a coating, the coating metal must wet and alloy with the substrate (e.g. lead does not wet steel and, hence, does not coat it – but a small addition of tin permits wetting, alloying and coating). The coating metal, as well as being of lower melting point, must not be too expensive and must confer desirable properties; corrosion resistance is the most important, but often the coated product is required to be formed and must have reasonable abrasion resistance. Commercial coatings of zinc, aluminium (and their alloys), and tin and its alloys are most important.

Steel is by far the most important basis metal. Cast irons are also coated by hot dipping, and some copper is coated with tin or tin alloys. Other hot-dip coatings are only applied for special purposes.

The dipping processes are of three basic types: (1) continuous lengths of strip, wire or tube pass through the molten coating metal; (2) semi-manufactured products such as cut tube lengths or sheets are dipped into the molten metal in batches in specially designed and automatically operated plants; and (3) fabricated products are dipped into the molten metal.

The coatings produced are designed to differ because with most semi-fabricated material, such as sheet, the final coating needs to be formed as easily as the basis metal, whereas on fabricated products this does not apply and thicker coatings with better corrosion resistance are provided. The vast majority of coatings are zinc based – more than twenty times as much zinc is used for hot-dip coatings as the total of all the other hot-dip metallic coatings. All three types of process apply for hot-dip zinc (galvanising) and zinc-5% aluminium coatings (Galfanising), although for fabricated products the zinc-5% aluminium alloy can be regarded as at industrial development stage. Hot-dip aluminium coatings (aluminising), while used in the past on fabricated products, are expanding now for continuously coated strip and also for wire. The 55% aluminium-43.5% zinc-1.5% silicon coating (Galvalume type) is used similarly for continuous coating of strip where the coating operation can be in a controlled atmosphere. Hot-dip tin coatings on

fabricated products are a significant market because they are non-toxic. Another important purpose of hot tinning is to facilitate the soldering of steel, copper, brass and other metals, e.g. copper wire is often tinned. With continuously coated steel sheet and wire, in addition to thick coatings, a major product is 'terne' an alloy of lead usually with 2–25% tin.

Principles of the Hot-dipping Operation

Some of the principles of hot dipping are common to galvanising, tinning, terne coating and aluminising.

Cleaning The surface must be cleaned of oil, grease and other surface contaminants and also of scale and oxide using degreasing and/or pickling treatments as required. The original Sendzimir pretreatment of steel strip by oxidation followed by reduction at high temperature, or other high temperature gaseous treatments developed more recently, eliminates the necessity for these operations and also for fluxing.

Retaining the clean surface until coating takes place and assisting reaction Keeping the material in a controlled atmosphere is often sufficient, but where exposure to air occurs (as with most coating of fabricated articles) a flux coating is usually applied to keep the surface clean and free from oxide. Fluxing may be by immersion in an aqueous prefluxing bath followed by drying, or by passage through molten flux floating on the bath of molten metal, or both of these. Molten flux attacks the surface, cleaning it and promoting the wetting of the basis metal by the molten metal into which it is dipped.

Dipping Strip or wire is coated continuously, often at high speeds. The continuous sheet plants have largely replaced cut sheet plants except in developing countries. Fabricated articles are dipped in batches mounted on suitable jigs if small, or singly if large, and the operation may be mechanised. Small articles and threaded work are dipped in perforated baskets suitable for subsequent centrifuging. Assuming that the article to be coated has been properly cleaned and fluxed, the basis metal and the molten coating metal interact on dipping, producing an alloy layer. If the article is colder on entry than the melting point of the coating metal, there may be a short intermediate stage when a solid skin forms around the article. Frequently, the basis metal (or article) is preheated to avoid this.

For any given pair of metals, the total amount of alloy increases with the duration of immersion and is also affected by the temperature of the bath.

The amount and nature of the alloy layer may be profoundly affected by additions to the molten bath, such as silicon to an aluminium bath, or aluminium to a galvanising bath. A change in the composition of the basis metal may also have a marked effect, e.g. mild steel containing a little silicon continues to react with zinc at a steady rate throughout immersion, whereas with steel without silicon the reaction rate decreases with time. Although the alloy layer is always referred to as if it were a single layer, it is usually made up of two or more layers corresponding to known metallurgical phases. Reaction can continue after the work has left the molten metal bath while the coating is solidifying and cooling.

After-treatments These include processes intended to produce one or more of the following results:

- (a) Reduction of coating thickness by reducing the amount of molten metal adhering to the substrate as it leaves the bath. Air or gaseous blasts or wiping techniques are used for continuous sheet and wire and for tubes. For fabricated articles this is usually done by centrifuging while the coating is still molten.
- (b) Improvement of the properties or appearance of the coating. Such treatments include quenching (to avoid unwanted alloy growth), chromating and phosphating and special treatments of both chemical and mechanical types for sheet.
- (c) Changing the character of the coating—as distinct from the more superficial treatments listed under (b). Hot-dipped zinc coatings are sometimes annealed to convert the whole of the coating into alloy as are aluminium coatings intended for heat resistance.

Design of Articles to be Hot-dip Coated

Co-operation between designer, fabricator and coater is essential if a satisfactory product is to be obtained. The design of any article required to be finished should take into account not only the function of the article and its method of manufacture but also the limitations imposed by the finish.

Galvanised coatings are extensively used to provide long-life protection to steel articles, such as structural steelwork, and building construction accessories. The coating thickness obtained in hot-dipping is largely determined by the steel composition with zinc coatings, but also by the rate of cooling and drainage of the coating metal from the article. The relatively thick layer of intermetallic compound produced by dipping steel in molten zinc is corrosion and abrasion resistant but cannot be produced. The alloy layer may be made very thin, such that the coating can be produced, by adding about 0.1–0.3% aluminium to the zinc bath, which is normal practice in sheet galvanising. Such coatings are only about 20% of the thickness of coatings on fabricated articles. The zinc coating also provides sacrificial protection.

Tin, or tin-lead coatings, only provide a corrosion resistant overlay and the basis metal, such as steel, exposed at pores in the coating is not protected. The intermetallic layer is not generally a significant proportion of the total coating thickness in the case of tin and tin-alloy coatings on steel. These coatings are frequently used to provide an easily solderable surface on different basis metals and have the virtue that the basis metal has already been wetted by the tin, or tin-lead, during the dipping process thus forming a metallurgical bond.

Mechanical assemblies may be made rigid by hot-dip processing since all crevices should be filled with the coating metal, and this will also provide a seal where required.

It is essential that the effect of heating of the basis metal during the hot-dipping process be borne in mind at the design stage, especially with aluminising when temperatures of about 700°C are reached and also with

galvanising where temperatures of about 450°C are used. High temperature can lead to the relief of any unbalanced stresses in the steel giving rise to distortion in some instances. A symmetrical design of parts will minimise this effect. Distortion can also arise where materials of substantially different thicknesses are used together in a fabrication since these will expand at different rates when heated. Corrosion fatigue resistance can be improved and other basis metal properties are little changed by hot dip galvanising. Changes in basis metal properties are unlikely to occur during hot dipping in tin or tin-lead, as the process temperature is lower.

Dipping in molten metal can also be extremely hazardous to workers if there is any danger of molten metal being thrown out of the bath. Molten metal must be able to enter and drain from fabrications without difficulty and this may require additional holes for venting and draining. Completely sealed compartments must not be immersed in molten metal since, if there is any liquid present, it will vaporise and may generate sufficient pressure to cause an explosion. Similarly, it is hazardous to immerse wet articles directly into molten metal because of the risk of spattering. Wet articles should be immersed through a flux cover on the bath surface.

Zinc and aluminium coatings are applied by hot dipping on steel and cast iron but there is a significant use of tin and tin-lead alloy coatings on copper-base materials, as well as on ferrous articles. Galvanised steel can readily be welded by all the processes used for bare steel but welds on tin-coated steel may be embrittled. Hydrogen embrittlement is not a problem in hot-dip galvanising of normal strength steels since hydrogen absorbed by the component during pickling is expelled again at the temperature of the bath. Strain-age embrittlement can occasionally arise when susceptible steel has been severely cold worked but galvanising usually has little effect on mechanical properties.

On mating surfaces an allowance should be made for the thickness of the coating. For flat surfaces 1 mm is generally sufficient and on galvanised nuts and bolts the recommended practice is to galvanize the bolts full size and the nuts as blanks which are tapped out up to 0.4 mm oversize after galvanising.

Hot-dip Galvanising of Fabricated Articles

Cleaning and Pickling After any necessary degreasing, the articles are usually pickled in sulphuric or hydrochloric acid. The choice is generally made on economic grounds; sulphuric acid costs less but requires heating whereas hydrochloric acid can be used cold. Hydrochloric acid is usually used at a strength of about 14% by weight and sulphuric acid at 10–14% and a temperature of 60–80°C. Inhibitors are added to the acid so that when the rust and scale have been removed very little attack occurs on the basis metal.

Grit blasting may be used, for example, to clean castings which may have sand on them, to remove welding slag or paint, or to roughen the surface of the work to cause more vigorous reaction between the zinc and the iron and thus a thicker coating. After grit blasting, it is desirable to give a quick dip in dilute hydrochloric acid to remove loose products before fluxing and galvanising. Castings may alternatively be pickled in hydrofluoric acid or

molten caustic soda, but these methods are not widely used as the chemicals are extremely hazardous to the operators.

Fluxing There are three fundamental processes used in galvanising of products which are known as the 'old dry', 'dry' and 'wet' methods but these may be modified or combined in individual cases. In the specialist strip and wire processes which are briefly described below more fundamental modifications are adopted.

The 'old dry' process involves pickling in hydrochloric acid and drying the work so that the pickle salts on the surface act as a flux when the work is dipped in the molten zinc. Otherwise the material, after pickling and rinsing, is either prefluxed, i.e. immersed in a tank of flux and then passed through a drying oven before dipping into the zinc (the dry process), or it is moved direct from the rinsing tank to the galvanising bath which has a 'blanket' of molten flux floating on the surface of the zinc (the wet process).

For prefluxing, a solution of zinc ammonium chloride ($\text{ZnCl}_2 \cdot 3\text{NH}_4\text{Cl}$) may be used at a strength of approximately 30% and a temperature up to 80°C; a wetting agent is generally added. Proprietary fluxes are also available. There should not be undue delay before dipping in the molten zinc or the flux coating will become less effective. Drying should not give a surface temperature in excess of 150°C or the flux will begin to decompose.

Flux blankets may be made from zinc ammonium chloride or from ammonium chloride plus frothing agents such as glycerin, tallow or sawdust. These thicken the blanket and lower the surface temperature thus reducing the volatilisation losses of ammonium chloride and the amount of fume which is generated.

Some galvanisers use both a preflux and a flux blanket since this cuts out the drying operation between prefluxing and galvanising and leads to greater productivity.

Galvanising When a clean iron or steel article is dipped in molten zinc a series of iron-zinc alloys is formed by reaction of the zinc with the surface of the article and, as it is removed from the bath, some of the molten zinc is taken out on top of the alloys.

At the normal galvanising bath temperature of 445–465°C, the reaction between iron and zinc is usually parabolic with time, so that the rate of reaction is rapid at first but then slows down.

The conditions which affect the type of reaction are bath temperature and the composition of iron or steel which is being coated. At 480–520°C the reaction between iron and zinc can be linear with time so that the thickness of the alloy layers will increase in direct proportion to the immersion time and the reaction will continue to be relatively rapid. With some steels (e.g. some silicon-killed steels), the reaction can be linear at the normal galvanising temperature of about 450°C.

The purity of the zinc used in the galvanising bath is not critical. Grades which contain just over 1% lead are usually used; indeed, lead is essential to avoid operational problems. Lead is soluble in molten zinc up to about 1%, but slab zinc containing a higher percentage of lead is helpful as the excess lead separates and prevents dross from sticking to the bottom of the bath and thus aids its removal. Aluminium is often deliberately added in very small quantities (about 0.005%) to brighten the appearance of the work

and give a smoother coating. The virtual absence of aluminium allows much greater thicknesses of coating to form than in sheet galvanising, the additional thickness being the iron–zinc alloy layers. Modern steel continuous casting processes often give residual silicon in the steel (or silicon is added as an alloying element) and still thicker coatings form. These can be controlled, e.g. by about 0.06–0.08% nickel in the galvanising bath. While most galvanising still takes place at 450–460°C, a high temperature (530–560°C) process is used for thin uniform coatings, particularly on threaded work.

Galvanising baths are generally constructed from special mild steel boiler plate having very small amounts of trace elements so that they are not rapidly attacked by molten zinc but they can be made of ceramic materials and heated from the top or by immersion heaters.

Threaded components and small articles on which excess zinc would interfere with their intended use, or which would otherwise stick together, are galvanised in perforated baskets which are transferred to a centrifuge and spun. This procedure for galvanising small parts is sometimes referred to as ‘spin galvanising’.

Steel tube and pipe are galvanised in plants with modern handling devices for automatic submersion and magnetic rollers for extraction from the zinc bath. At this stage, the tubes are passed through a compressed air ring and the insides are given a blast of high pressure steam to clean the surface and give a uniform coating. Otherwise, the process is similar to the galvanising of fabricated articles.

Quenching is essential if the work has been withdrawn through a flux blanket to avoid staining of the surface by flux residues. It also cools the work quickly, preventing the alloy layers on reactive steels from continuing to grow after the work has been removed from the bath, limiting surface oxidation and enabling articles to be handled more readily. Chromic acids or chromate salts may be added to the quench water to prevent wet storage stain (white rust). Chromating is also advantageous for galvanised steel reinforcement for concrete. Phosphating of the galvanised surface is a good base for powder or paint adhesion.

Continuous Zinc and Zinc-alloy Coating

Large tonnages of wire and sheet in coil form are continuously galvanised on automated lines. In the past twenty years, the greatest developments in hot dipping relate to techniques and materials used in coating sheet steel with zinc and zinc alloys.

Surface preparation is now by gaseous treatments in most strip lines and some wire lines: pickling remains usual for products and tubes which are less easily passed through sealed chambers containing closely controlled gaseous mixtures. Originally, oxidation/reduction techniques were used (Sendzimir), but since the mid-1960s, more intense heating in a slightly reducing atmosphere has often replaced the initial oxidation so that less hydrogen is needed in the reducing stage. A third alternative with limited use is electrolytic alkaline cleaning (US Steel process) often coupled with annealing. Chemical cleaning and fluxing (Weirton process) also has limited use.

The sheet is fed into the galvanising bath through a snout which dips below

the surface of the molten zinc and protects the surface of the steel against re-oxidation; this eliminates the need for fluxing. The strip enters the molten zinc at a temperature of 470–480°C and most of the heat required for the galvanising bath is supplied by the sheet itself.

Hot dipping in a controlled atmosphere gives greater process control by avoiding surface oxidation which is needed with the zinc alloys containing high aluminium contents, but experience has shown that sheet can be coated with zinc–5% aluminium in air. Development of fluxes so that more complex shapes can be coated with zinc–aluminium alloys in air is in progress; this will also facilitate processes in which zinc is pumped over the steel instead of the steel being dipped—at present such processes, which are used for external coating of small diameter tubes, require the use of an inert atmosphere.

The continuous coating of steel strip with zinc no longer aims at an attractive spangled finish as, when painted, the outline of the grain boundaries remains visible through the paint. No spangle or minimum-spangle allows a simple paint coating to be applied and to have good specular reflectivity without the substrate structure being visible. This is achieved by sweeping the coating before solidification with narrow jets of steam or air stretching the width of the sheet and by depositing a large number of crystallisation nuclei on the surface just before solidification; 5 µm zinc dust is widely used for this purpose. A skin-pass after solidification is an alternative method used for sheet which is to be continuously painted. Paintability (and weldability) is also improved by converting the surface to a zinc–iron alloy (galvannealing) in line.

User demands, particularly from the car industry, have led to developments in which different thicknesses of coating applied to each side of the sheet, or one side is completely uncoated. Maximum zinc is needed to combat corrosion by road muck and salt on the inside of the car body sheet which is not easily cleaned. Corrosion rarely starts from the exterior of the car which is regularly cleaned and, hence, the low-zinc or no-zinc surface is preferred as being the best base for a smooth paint finish. One-side coating techniques include: (1) passing the steel sheet close to the molten zinc surface and using surface tension effects (meniscus coating) to hold a layer of zinc in contact with the steel; (2) shielding one side; (3) coating normally and then electrolytically transferring the zinc from one side to the other.

Steel wire is also galvanised on a continuous basis and the principles of the Sendzimir sheet galvanising process and later developments have been applied as an alternative to wet cleaning and pickling. The mechanical requirements of the coated product may determine both the type of steel used and the coating process. With certain grades of wire, the required tensile strength can only be obtained by drawing the wire after it has been coated and in these cases the coating may be applied by electroplating.

For annealed wire, the strands of wire are first taken through a bath of molten lead, where the desired softening is achieved and this process also has a partial cleaning effect. The strands are then pickled, fluxed and galvanised. An even coating is obtained by wiping the wire after galvanising and this helps to control the coating thickness which is also affected by the angle of withdrawal from the galvanising bath. For the heavier coatings, the wires are drawn through a bed of charcoal and for thinner coatings wiper pads are held against the wires by various methods.

Hot tinning

Iron and steel

Hot dipped tin coatings, like galvanised coatings, have practical thickness limits and possess an under-layer of intermetallic compound, usually described as the alloy layer.

In processing articles, after degreasing in trichloroethylene vapour or electrolytically in a hot alkaline solution, e.g. 25 g/l trisodium phosphate and 12.5 g/l sodium carbonate at 80–90°C, they are pickled in 50% v/v hydrochloric acid at ambient temperature or 5–10% v/v sulphuric acid and rinsed. The surface of cast iron is often contaminated with sand from the casting process and normal pickling processes cannot deal with this. The addition of some HF to a sulphuric acid bath helps to remove a siliceous skin. Making the pickling process more severe or more prolonged often makes matters worse because the sludge and smut left on the surface by the pickling action are increased. The simplest cleaning method is by fine grit blasting after which the iron may be fluxed and tinned directly. Tinning trouble due to graphite may be overcome by rough mechanical cleaning followed by electrodepositing a thin coating of iron or copper. Alternatively, the graphite may be removed, either by surface decarburisation (as in malleable cast iron) or by treatment in molten salt baths, e.g. equal parts of sodium and potassium nitrates. The nitrate salts are then washed off and the article is lightly pickled, rinsed and fluxed in the usual way, e.g. by dipping in an aqueous flux solution containing, for example, 240 g/l zinc chloride, 60 g/l sodium chloride, 30 g/l ammonium chloride and 6–12 ml/l hydrochloric acid (sp. gr. 1.14). The articles, wet with flux solution, are lowered carefully into a bath of molten tin (at about 280°C) having a layer of fused flux floating on it and covering about two-thirds of its surface. The flux cover is composed of a mixture of dry chlorides in the same proportions by weight as in the flux solution being carried over with the work. Thus, in the example given, finely ground zinc, sodium and ammonium chlorides are mixed in the proportions 8:2:1 to form the flux blanket.

When the article has attained the temperature of the tinning bath, the flux cover is drawn to one side of the bath with a paddle and the article is immediately withdrawn through the flux-free area of the tin surface. The quality of the coating may be improved by dipping the tinned article into a second tinning pot in which the tin is covered with a layer of molten grease such as tallow, and is at a temperature of 240–270°C.

Small articles may be tinned in batches, on jigs or in baskets, and then spun in a heated centrifuge to remove excess tin. The brightness of the tin coating may be preserved by quenching the articles in a layer of paraffin or white spirit, 50–100 mm thick, floating on water. Small parts can be separated from one another, before the tin coating solidifies, by allowing them to fall on to a paddle wheel rotating at 500–1 000 rev/min.

Hot tinning of individual sheets has largely been replaced by electrolytic tinning lines processing continuous strip. Hot tinning of narrow strip has a limited production. Electrolytic pickling in dilute sulphuric acid is usual after electrolytic alkaline degreasing. In sheet tinning, the work passes downwards through a layer of molten zinc chloride flux into the molten tin at

300–320°C. On emerging, the sheets pass through pressure rolls in palm oil at 240°C to remove tin.

A hot-dipped tin coating on steel has a layer of FeSn_2 at the interface between the tin and the steel. This alloy grows very slowly in comparison with the more complex alloy layers formed in galvanising and in aluminising. It usually comprises 10–20% of the total coating thickness.

Tin-lead coatings containing 2% or more of tin may be applied by hot-dipping to steel, copper and copper alloys. Steel sheets are commonly coated with alloys containing 7%, 10% or 25% tin; these are called *terne plate* with the name tin-terne sometimes applied to the higher tin content coating. The initial cleaning in the British Steel plant at Cookley is in a ferric chloride/hydrogen peroxide/hydrochloric acid solution, which etches the surface and nickel electroplating precedes *terne* coating, which is used for safety-critical products such as car fuel tanks. Alternatively, the tin content may only be 2% and such coatings are described either as *terne* or as lead coatings. Antimony up to about 5% is an alternative to tin in hot-dipped lead baths. The coating process is essentially similar to tinning. However, it is necessary to choose the bath temperature to suit the freezing range of the particular alloy in use.

Copper

Degreasing by cathodic treatment in a hot alkaline solution is desirable when the copper contains inclusions of cuprous oxide. Pickling may be carried out in either cold 50% hydrochloric acid or 20% v/v nitric acid, or in hot (70°C) 6% v/v sulphuric acid containing 1.5% w/w sodium dichromate.

An aqueous solution of zinc chloride, acidified with hydrochloric acid, may be used as a flux. A light flux cover is used on the tinning bath and this is normally produced and maintained by the carry-in of flux solution on the work. The bath temperature should be 250–260°C. Bright annealed copper wire may be fluxed in stannous chloride and tinned at 300°C; excess tin is wiped off by pulling the emerging wire between lightly clamped rubber blocks.

Alloy formation is faster on copper than on steel and tends to be more irregular. With coating thicknesses of 1 μm or less, the thickness of the alloy layer may amount to half that of the complete coating. It consists of a thin layer of Cu_3Sn adjacent to the copper and a thicker layer of Cu_6Sn_5 adjacent to the tin.

The process of flow-brightening of tin coatings also requires mention. Matt electrodeposited coatings may be brightened by momentary fusion. This process of flow-brightening or flow-melting is achieved with most of the electrolytic tinplate production by conductive or inductive heating. For manufactured articles, it is usually carried out by immersion in a suitable hot oil or vapour or by infra-red treatment. The flow-melted electrodeposited coatings develop an alloy layer, which is somewhat thinner than that obtained in hot dipping, but increases in thickness with time.

Hot-dip Aluminising

Although hot-dip aluminising of sheet might appear to resemble hot-dip galvanising very closely, there are several important differences which combine to make the process more difficult to operate. The main difficulties are:

1. The melting point of aluminium (660°C). The operating temperature usually reaches 750–850°C in pretreatment and 700°C in the bath, causing a loss in tensile properties of cold-drawn wire. On the other hand, if cold-worked material which is to be subsequently annealed is used in this process the annealing and coating operations may be combined, with obvious economic advantage.
2. Very rapid reaction occurs between molten aluminium and iron. This leads to rapid alloying and increased dross formation. A ceramic-lined container is desirable.
3. Fluxing is much more difficult with aluminium than with tin and zinc.
4. The oxide layer on molten aluminium, though thin, is most tenacious. Any article leaving the bath is liable to be contaminated with streaks of this oxide or with globules of metal entangled in the oxide film.

The main process use is in the continuous aluminising of steel strip. The cleaning section usually uses reducing gases to convert iron compounds on the strip surface to metallic iron. In many modern lines, as for zinc, the reducing furnace is preceded by a non-oxidising open-flame furnace which heats the strip rapidly to a temperature close to that of the reducing furnace. The slightly reducing atmosphere achieved by controlling combustion conditions allied to the swirling flow of the combustion product gases in contact with the strip combine to produce some cleaning before the reducing furnace is reached. The latter operates with a strongly reducing atmosphere of, for example, cracked ammonia. The heating in this furnace is usually achieved with radiant tubes which maintain the furnace at 750–850°C.

After gaseous cleaning, the strip cools slightly as it passes through a narrow box section, whose end is sealed by the molten aluminium of the aluminising bath, into the dipping section.

The bath is normally at a temperature in the range 620–710°C, depending on whether the coating material is an aluminium–silicon alloy (for use in high-temperature conditions) or pure aluminium (for corrosion prevention). It is heated by inductors, by resistance heaters or by an external flame. The pot will usually be refractory lined unless cast-iron pots are needed to ensure adequate heat transfer from an external flame. As molten aluminium is extremely aggressive towards ferrous metals, replacement of cast-iron pots is fairly frequent. Refractory-lined pots obviously do not have this drawback, although the bath hardware, in particular the sinker roll and support mechanism, will still be attacked and need replacement at intervals.

Subsequent treatment such as air-knives and chromating are similar to galvanising lines.

Fabricated articles are less commonly hot-dip aluminised now than in the past. Coatings are applied after cleaning the work, e.g. pickling in hydrochloric acid in the case of steel and then preheating. The work is then immersed in a molten salt bath, a flux or reducing atmosphere, prior to

immersion in the bath of molten aluminium. Alloying occurs between iron and aluminium at the interface.

Two commercial grades of aluminised steel sheet are produced. Type 1 aluminised steel is coated with an aluminium-silicon alloy containing typically 5–11% silicon, whereas the type 2 grade is coated with a heavier layer of 'pure' aluminium, although heavier aluminium-silicon coatings are sometimes referred to as 'type 2'. A disadvantage of silicon-containing aluminium coatings is that they darken when subjected to atmospheric corrosion. Beryllium produces the same results as silicon and is much more effective, under 0.1% being sufficient to halve the alloy thickness, but its toxicity and greater cost have hindered its commercial use. Although the influence of numerous other elements has been investigated, nothing has been found to equal the results obtained with beryllium and silicon.

With the type 1 grade of aluminised steel the total coating thickness, including the alloy layer, lies in the range 14–25 μm (80–150 g/m² including both sides), whereas the coating thickness on the type 2 grade is normally in excess of 40 μm (230 g/m² including both sides). In both cases, about 2–4% of iron is present in the coating alloy. This is iron dissolved from the strip and the coating bath hardware. An alloy layer containing intermetallic compounds can be seen between the coating layer and the steel substrate in both grades. This layer is thicker in the type 2 grade in which it mainly comprises Fe_2Al_3 . As intermetallic compounds are generally very brittle, it is desirable to keep the alloy layer fairly thin. The addition of silicon achieves this aim, producing a slightly different alloy layer morphology and structure. In this case, a mixture of FeAl_3 and Fe_2SiAl_3 forms. The alloy layer in both grades thickens with time and temperature at a rate which is generally parabolic, but there is a slower rate of thickening of the alloy layer in the type 1 grade, probably attributable to a combination of a larger dissolution rate and a slower solid state growth rate.

'Post-annealing', which involves an overaging heat treatment carried out for about an hour in the temperature range 400–500°C can be used to increase material ductility slightly. A coating which has a total thickness of 25 μm , in which the alloy layer occupies about 25% of the total, has satisfactory bending properties. Excessive deformation during forming can lead to cracking of the alloy layer and even de-lamination of the coating. The thicker alloy layer on the type 2 grade tends to crack more readily than that on type 1. Thus, particular care should be taken in specifying bend radii when aluminised steel is to be used for a pressing, particularly in the case of the type 2 grade.

Aluminised steel has far better heat resistance than galvanised steel, maintaining a bright metallic surface on exposure to temperatures up to approximately 500°C for long periods of time. Higher temperatures will eventually lead to the conversion of any free aluminium at the surface to iron-aluminium compounds and solid solutions of aluminium in iron. Exposure at temperatures up to 700°C is possible without promoting catastrophic breakdown of the steel substrate. In addition, aluminised steel does not suffer from the intergranular embrittlement problems arising from intergranular diffusion of zinc reported for galvanised steel at high temperatures. Galvalume, a strip product coated with an alloy containing 55% Al, 43.5% Zn and 1.5% Si, has also been reported to suffer from intergranular

embrittlement at temperatures close to 500°C, although this can be prevented by increasing the phosphorus content of the substrate steel above 0.04%. Aluminised steels with even better high temperature properties have also been produced. Their claimed elevated temperature resistance improvement is said to be due to the presence in solution in the steel substrate of elements which promote higher elevated temperature strength and control the tendency of the standard aluminised coating to spall off under severe conditions.

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12.3 Principles of Applying Coatings by Diffusion

General

Since corrosion is a surface reaction, all types of protective coating must involve a change in the surface composition of the metallic component. This change can be brought about by addition of a different material, metallic or otherwise, applied in the form of an outer 'skin', which provides a barrier between the body of the component and the surrounding corrosive medium. This form of coating is by far the most common; it includes paints, varnishes, enamels, plastics, and metals applied by electroplating, hot dipping, flame spraying etc.

It is also possible to modify the chemical composition of the surface to be protected by diffusing into it a suitable metal or element which in combination with the parent metal or alloy will provide the required resistance to the corrosive medium. Such surface alloys are called *diffusion* coatings. 'Surface alloying' would probably be a more correct designation since the modified surface layers are in fact an integral part of the component and cannot be stripped off the parent metal as could a paint film or an electroplated metal deposit. The dimensional change in the protected article is less than the thickness of the effective surface alloy, and may be negligible. The term 'coating thickness' is usually applied to the surface alloy as revealed by suitable etching (Fig. 12.17). Often there is a convenient metallographic feature which is taken as the limit of the coating thickness although the coating element has diffused deeper at low concentration, as can be shown by chemical analysis and more recently by electron micro-probe studies.

These properties of integration with the underlying metal and negligible dimensional change are the most important features which distinguish diffusion coatings from other types of protection.

Metals Usually Applied by Diffusion

So far, few of the commercially operated diffusion processes have been applied to the lower-melting-point metals. While they are being used to an increasing extent for protection of nickel, cobalt and refractory alloys, the bulk of present-day applications is still concerned with the treatment of ferrous materials.

Table 12.3 has been compiled in order to give a general idea of the field covered by diffusion processes. Chromium diffusion (*chromising*), which has been applied for the purposes of resistance to corrosion, thermal oxidation and abrasion, is probably one of the most versatile forms of diffusion coating, and has been much more extensively studied than the other processes. Reference may be made to several general accounts of diffusion coatings^{1,2} and chromising³⁻⁷; papers on specific aspects are indicated where appropriate. Drewett's review⁸ has a good bibliography covering aluminium, chromium and zinc diffusion coatings.

Zinc diffusion (*sherardising*)⁸⁻¹¹ is mainly used for protection of ferrous metals against atmospheric corrosion. It has, in some respects, properties related to other types of zinc coating such as galvanising, but owing to the small dimensional change involved, it is of particular value for the treatment of machined parts, bolts, nuts, etc.

Aluminium diffusion (*calorising*, *aluminising*)^{8,12,13} protects steels against oxidation at elevated temperatures, and the more recently developed processes for aluminising and chromaluminising 'superalloys' are widely used to increase the life and operating temperature of aircraft gas turbine vanes, etc.

Table 12.3 Diffusion processes

Coating element(s)	Substrates	Properties obtained or improved	Stage of development	References
Al	Cu and alloys	Th.ox.	Com.	8, 12, 13
	Fe, steels, cast iron	Th.ox.	Com.	
	Nb, Ti and alloys	Th.ox., frict.	Exp.	
Al, Al + Cr	Stainless steels	Th.ox.	Com.	2, 35-43
	Superalloys*	Th.ox., th.corr.	Com.	
	Fe, steels, Ni- and Co-alloys, Mo	Hard., th.corr.	Com.	
B	Fe, steels, cast iron	Corr., th.ox., hard.	Com.	1-8
B(+others)		Corr., th.ox., frict.	Com.	
Cr		Th.ox., th.corr.	Com.	
		Th.ox.	Com.	
	Stainless steels	Corr., th.ox., frict.	Com.	4, 33
	Ni and alloys	Th.ox., th.corr.	Com.	
	Mo, W and alloys	Th.ox.	Com.	1
Cr + Al, Si, Zr, etc.	Steels	Th.ox. (higher temp.)	Com.	
	Superalloys*	Th.ox., th.corr.	Com.	40
	Mo	Th.ox.	Com.	
Mo	Steels, stainless steels	Special corr.	Exp.	34
Mo, Mo + Cr	Ni and alloys	Corr. (acids)	Exp.	
Si	Fe, steels	Corr. (acids), hard.	Com. (USA)	14, 15
Si (+others)	Mo, W, Nb, Ta	Th.ox.	Com.	
Ta	Ni alloys, superalloys*	Pretreatment for chromising, etc.	Exp.	40
		Hard., pretreatment for chromising	Com.	
Ti	Steels, Ni alloys	Hard., pretreatment for chromising	Com.	8-11
Zn	Fe, steels	Corr.	Com.	
	Nb	Th.ox.	Exp.	47

Abbreviations: Corr. = resistance to corrosion

Frict. = low friction, anti-galling

Hard = hardness, resistance to abrasion

Th.corr. = resistance to thermal corrosion (e.g. sulphidation)

Th.ox. = resistance to thermal (high temp.) oxidation

Com. = commercial; Exp. = experimental

*Superalloys: high temperature creep-resisting alloys based on Ni, Co, and including (here) the Nimonic series.

Silicon diffusion (*Ihrigising*)^{14, 15} is not commonly applied to steels, but is increasingly used to protect the refractory metals^{2, 16} (*disilicide coatings*).

Mechanism of Coating Formation

Diffusion coatings are formed as a result of interaction of two distinct processes; the solute metal is brought into contact with the surface of the solvent, and this is followed by diffusion proper which consists in the gradual absorption of the solute into the lattice of the solvent.

Whatever method is used to provide an adequate supply of diffusing metal, the diffusion mechanism remains identical for any given solute/solvent system, and it is appropriate to discuss the diffusion aspect in the first place.

Theory of Diffusion¹⁷⁻¹⁹

Diffusion is a process whereby the distribution of each component in a phase tends to uniformity.

For such a condition of equilibrium to be reached, the atoms must acquire sufficient energy to permit their displacement at an appreciable rate. In the case of metal lattices, this energy can be provided by a suitable rise in temperature. In the application of coatings the diffusion process is arrested at a suitable stage when there is a considerable solute concentration gradient between the surface and the required depth of penetration.

In metals, the distance between the individual atoms in the lattice is of the order of 0.4 nm and only atoms of very small size are able to penetrate interstitially. This takes place, for instance, in the diffusion of hydrogen into iron, and of carbon into austenite, etc. This type of interstitial diffusion is usually rapid, since the inward movement of the solute atoms is relatively unhampered.

Interstitial diffusion is rarely possible when two metals interdiffuse, since their atomic radii are usually of the same order. Several mechanisms have been proposed, but it is now generally accepted that interdiffusion is due to the motion of vacant sites within the lattice, solvent and solute atoms moving as the vacant sites migrate. The diffusion process is thus dependent upon the state of imperfection of the solvent metal and the alloy being formed.

The kinetics of the diffusion process (whether interstitial or substitutional) can be expressed by Fick's equations:

$$P = -D \frac{dc}{dx} \quad (12.13)$$

where P is the rate of permeation of solute (e.g. coating metal) through a unit of the solvent metal in the direction x , D is the diffusion coefficient and c is the concentration, and

$$\frac{\partial c}{\partial t} = D \frac{d^2 c}{dx^2} \quad (12.14)$$

which expresses the rate of increase of concentration at any point (when D is independent of concentration).

For diffusion into semi-infinite solids, the depth of diffusion is related to the time t by the equation

$$x^2 = 4kDt \quad (12.15)$$

where k is a constant which is determined by the concentration at the surface and at a depth x .

The diffusion coefficient varies with temperature according to the following Arrhenius-type equation:

$$D = D_0 \exp[-E^*/RT] \quad (12.16)$$

where T is the absolute temperature, R is the gas constant, E^* the energy of activation and D_0 the diffusion or frequency factor.

It must be noted that the values of D_0 and E^* are influenced by the concentration of the solute metal and also by the presence of alloying elements in the solvent. It has also been shown that the diffusion coefficient for a given solute is in inverse proportion to the melting point of the solvent. D is least for metals forming continuous series of solid solutions and for self-diffusion.

Strictly the diffusion coefficient D measured for any type of binary system A/B is in fact the resultant effect of two partial diffusivities D_A and D_B , representing respectively the diffusivity of A into B and of B into A . For most practical purposes, however, a single diffusion coefficient is sufficient to define a given diffusion system.

Methods of Deposition

As mentioned earlier, the diffusion process depends on an adequate supply of solute metal at the surface of the solvent. So long as such a supply is available, the diffusion will proceed at a rate which, as shown above, is largely determined by the temperature selected for the process. Various methods of providing this supply may be employed. A metal may be electrodeposited on another metal, and the coated material may be subsequently heated at a temperature sufficient to effect diffusion. This method has the disadvantage of requiring two operations. Another method consists in heating the solvent metal in the presence of the solute metal in powder form (sherardising when zinc is the coating metal, and calorising when aluminium forms the coating). This technique, designated by the general name of cementation, is mainly applicable to the diffusion of low-melting-point metals.

Solid-solid diffusion Sherardising is a good example of a solid-solid diffusion process. The iron or steel articles, after thorough degreasing and pickling, are packed in a powder containing zinc dust and a diluent such as silica or sand. The powder and articles are then placed in a steel drum which is slowly rotated while the temperature is raised to between 350 and 400°C, i.e. below the melting point of zinc. The temperature is maintained for 3–10 h depending on the size of the components and on the coating thickness required.

Usually, rapid cooling is obtained by removing the drum from the furnace and spraying it under a water jet while rotating slowly.

Substantially all the zinc is absorbed by the surface of the components, and the resulting coating has a matt-grey appearance and consists essentially of a zinc-iron alloy averaging 90–95% Zn. If excess zinc is made available and the treatment is prolonged, pure zinc is deposited at the surface.

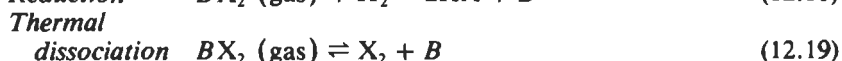
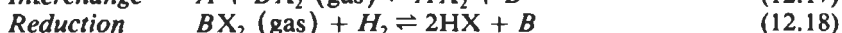
Temperatures well in excess of 400°C can be used for processing; in this case much deeper coatings are obtained, but the iron content of the surface alloy is higher and the diffusion layer is very brittle and less corrosion-resistant. This effect is easily explained when it is remembered that the rate of interdiffusion is far more rapid when the temperature is above the melting point of zinc (420°C).

Although zinc has an appreciable vapour pressure at the temperatures of treatment, it is unlikely that zinc vapour plays any significant part in the diffusion process and it is generally accepted that the mechanism relies almost exclusively on intimate contact of finely divided zinc dust with the steel surface. In spite of this requirement, coatings of even thickness and composition are obtained on the most intricate shapes, on fine threads, inside blind holes, and in the bore of small-diameter tubes. Large articles of uniform section, e.g. rods, tubes, etc. can be coated by this process.

Zinc diffusion produces slight dimensional changes, but the increase of thickness due to the addition of zinc is controllable and independent of the surface contours. This property which is common to most diffusion processes is of special value for the treatment of threaded parts and articles with intricate contours.

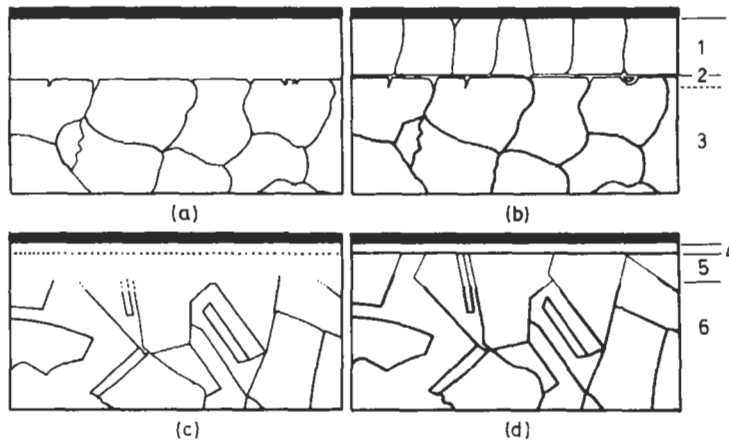
Gas-phase deposition In this process, a halide of the solute metal is passed in vapour form over the surface of the metal to be coated, which is heated to a temperature at which diffusion can take place. Temperatures of 500–1 300°C or more can be used, depending on the particular system considered. Generally, 'filler' atmospheres are provided to carry the halide vapour; these atmospheres are usually reducing gases such as hydrogen, cracked ammonia, etc. or inert gases (helium, argon).

Three main types of reaction can take place in which the metal halide, BX_2 , is reduced to metal B , which then diffuses into the solvent metal A . The following considerations, which have been confined to bivalent metals, are of general application.



The interchange reaction* implies the removal of one atom of A at the surface for each atom of B deposited. It therefore takes place with a minimum change in weight or dimensions of the article (A). If A and B have similar atomic weights, as in the case of iron and chromium, interchange reaction will produce little change in weight and no measurable increase in dimension, whatever the thickness of the diffusion layer.

* Reaction 12.17 might be considered as the result of two reactions, i.e. reaction 12.18 or 12.19 followed by reaction of HX or X_2 with A to form AX_2 .



LEGEND

- | | |
|---|---|
| 1. Columnar ferrite formed from austenite during chromising | 4. β -phase layer; apparently the 'coating' in (d) |
| 2. Boundary between coating and core, with intergranular diffusion into austenite of core | 5. α -phase coating, not etched by nitric acid [(c)] |
| 3. Core; ferrite formed from austenite on cooling | 6. α -phase core |

Fig. 12.17 Illustration of grain patterns for chromised low-carbon steel and nickel. (a) Chromised steel, etched with nital; (b) chromised steel etched with Marble's reagent; (c) chromised nickel etched with nitric and acetic acids; (d) chromised nickel etched with Marble's reagent

On the other hand, both reduction and thermal-dissociation reactions will result in an increase in weight (equivalent to the solute deposited) and a slight increase in dimensions which will depend on the average composition of the diffused layer.

The thermodynamics of interchange and reduction reactions are of particular interest, since knowledge of the feasibility 'areas' of these reactions is of great assistance in determining the best conditions of processing for any given system.

Some interesting conclusions can be drawn by plotting $\log K_p$ against temperature for thermal dissociation reactions of the type $M + \text{Cl}_2 \rightleftharpoons M\text{Cl}_2$ (M is any given metal). (See Fig. 12.18)²⁰.

The equilibrium constant K_p can be derived from the free energy equation

$$-\Delta G^\circ = 2.303 RT \log K_p \quad (12.20)$$

Considering B as a coating metal and A as the solvent, we have for

$$B + \text{Cl}_2 \rightleftharpoons B\text{Cl}_2, \quad K_{p,B} = \frac{p_{B\text{Cl}_2}}{a_B p_{\text{Cl}_2}} \quad (12.21)$$

$$A + \text{Cl}_2 \rightleftharpoons A\text{Cl}_2, \quad K_{p,A} = \frac{p_{A\text{Cl}_2}}{a_A p_{\text{Cl}_2}} \quad (12.22)$$

and for the interchange reaction,

$$B\text{Cl}_2 + A \rightleftharpoons A\text{Cl}_2 + B, \quad K_{p,1} = \frac{a_B p_{A\text{Cl}_2}}{p_{B\text{Cl}_2} a_A} = \frac{K_{p,A}}{K_{p,B}} \quad (12.23)$$

or

$$\log K_{p,1} = \log K_{p,A} - \log K_{p,B} \quad (12.24)$$

For coatings where $a_A \approx a_B$ at the surface, a difference of -1 unit in equation 12.24 means that approximately 10% of the chloride vapour has been converted into coating metal. A difference of -2 units represents a conversion of approximately 1%, which we can regard as a minimum required for practical interchange reaction, in a continuous flow system. On this basis, it can be seen from Fig. 12.18 that chromising falls within the limits of feasibility, and that siliconising and stannising of iron should proceed even more efficiently, as is in fact borne out experimentally. Chromising of nickel or of molybdenum should not be possible by interchange reaction since the difference is well over -2 units, and in fact interchange does not occur.

The feasibility of the reduction reaction can be considered by a similar method.

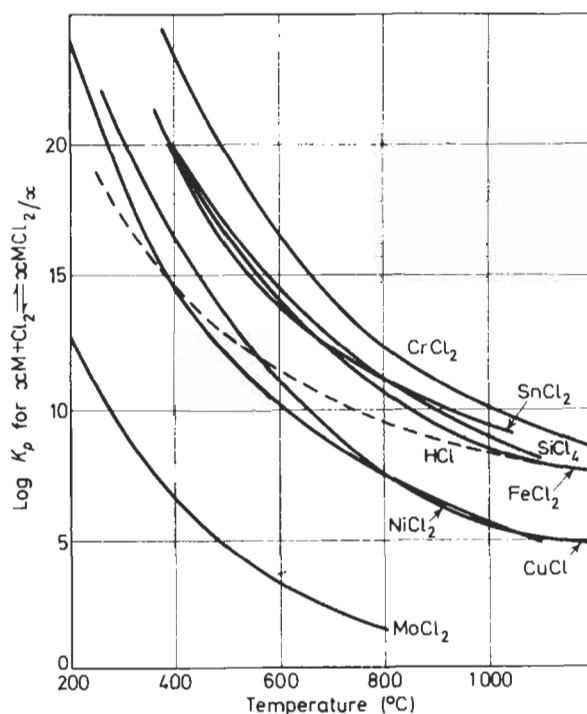


Fig. 12.18 $\log K_p$ for $xM + \text{Cl}_2 \rightleftharpoons xM\text{Cl}_2/x$ [after *Aust. Eng.*, Dec., 63 (1950)]

For $\text{H}_2 + \text{Cl}_2 \rightleftharpoons 2\text{HCl}$,

$$K_{p, \text{H}_2} = \frac{p_{\text{HCl}}^2}{p_{\text{H}_2} p_{\text{Cl}_2}} \quad (12.25)$$

For the reduction $\text{BCl}_2 + \text{H}_2 \rightleftharpoons 2\text{HCl} + \text{B}$ we have

$$K_{p, R} = \frac{a_B p_{\text{HCl}}^2}{p_{\text{BCl}_2} p_{\text{H}_2}} = \frac{K_{p, \text{H}_2}}{K_{p, B}} \quad (12.26)$$

or

$$\log K_{p, R} = \log K_{p, \text{H}_2} - \log K_{p, B} \quad (12.27)$$

p_{H_2} is equal to 1 if hydrogen is at atmospheric pressure. If no interchange occurs, $a_B \approx 1$. The reduction reaction will proceed effectively if $\log K_{p, B}$ is not more than 1 or 2 units greater than $\log K_{p, \text{H}_2}$. Thermal dissociation is not feasible, except for iodides.

In many instances, more than one type of reaction can take place at any given temperature. When the reduction reaction plays an important part, it is usually possible to alter the composition and characteristics of the coating by controlling the hydrogen supply to the reaction chamber.

When the coating metal halide is formed *in situ*, the overall reaction represents the transfer of coating metal from a source where it is at high activity (e.g. the pure metal powder, $a_A = 1$) to the surface of the substrate where a_A is kept less than 1 by diffusion. The formation of carbides or intermetallic compounds such as aluminides or silicides as part of the coating reaction may provide an additional driving force for the process.

The reactions work both ways, and constituents of the alloy being coated may be removed by the halide atmosphere even when 'interchange' does not occur. For example, a nickel-chromium alloy may be superficially dechromised by nickel powder in a chloride atmosphere. Thus loss of important alloying constituents may have to be controlled during diffusion coating processes.

Molten bath deposition The interchange reaction also takes place when the coating metal halide is dissolved in a fused salt²¹. Alternatively, deposition may be by electrolysis²². Another technique uses the coating metal dissolved in molten calcium²³.

Chromising offers a good example of the types of reaction involved and of the general characteristics of diffusion coating.

Chromising as an Example of Diffusion Coating

Most modern methods of chromising rely on the reaction of a chromium halide at the surface of the metal to be coated. Three main methods are commercially operated.

Purely gaseous method²⁴⁻²⁶ Articles are suitably jigged inside a retort chamber and vapours of chromium halide, usually diluted with a reducing gas, are circulated. The temperature is maintained within the range 950–1 200°C for chromising of iron and ferrous alloys (recent Russian work on

vacuum chromising utilises chromium metal vapour derived from ferrochromium in a vacuum furnace together with the articles being coated, at about $1\,350^{\circ}\text{C}^{27}$).

Semi-gaseous method The articles, surrounded by a solid 'compound' containing chromium metal, are packed in a retort chamber, and vapours of chromium halide or halogen compound are circulated in the chamber, which is maintained at 950 – $1\,200^{\circ}\text{C}$.

Pack method The articles are packed in a 'powder compound' containing chromium metal or ferrochrome and a source of halogen in solid form, e.g. NH_4Cl , NH_4Br , NH_4I . Gas-tight boxes fitted with suitable sealing fixtures are used. The range of temperatures is the same as in the other two methods.

It is usual to treat low-carbon steel between 980 and $1\,050^{\circ}\text{C}$, although the process is operable within the temperature limits stated above. Techniques based on all three methods, and on the use of fused salts, have been proposed for the treatment of steel in coil form²⁸.

The iron-chromium constitution diagram is shown in Fig. 12.19. At around $1\,000^{\circ}\text{C}$, it can be seen that when chromium is deposited and diffused

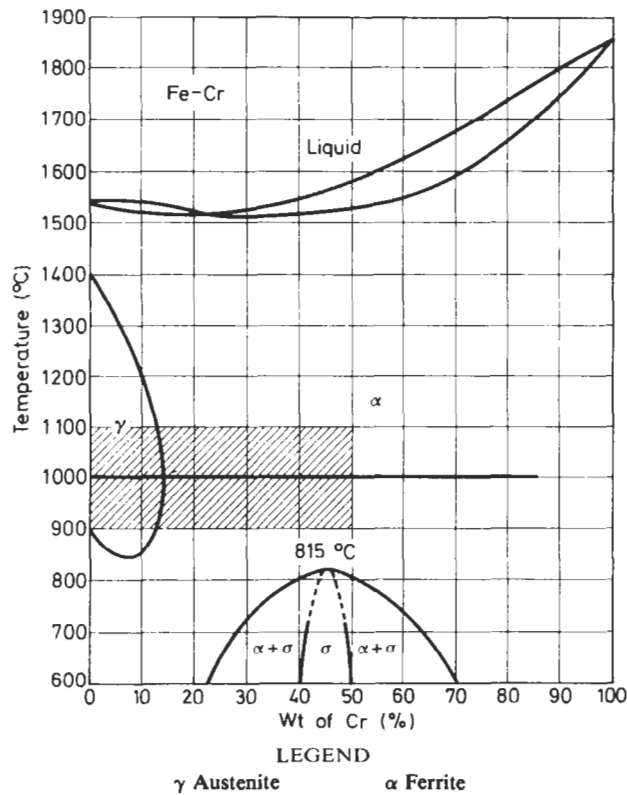


Fig. 12.19 Iron/chromium diagram

inwards, the austenite structure of the steel remains unchanged until a concentration of approximately 12% chromium is reached. At higher chromium concentrations, the structure becomes ferritic. Since the rate of diffusion of chromium is greater in ferrite than in austenite, there is a rapid rise in the chromium concentration of the coating which is only partly offset by the slow diffusion beyond the 12% Cr boundary. As a result, there is a sharp concentration drop at the ferrite/austenite boundary. Grain boundary diffusion occurs³⁰, but has little effect on the coating thickness.

The chromium concentration as a function of distance from surface is shown in Fig. 12.20. The 12% chromium boundary (broken line) represents

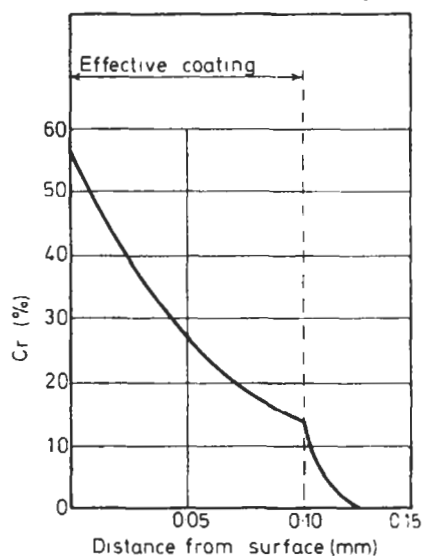


Fig. 12.20 Chromium concentration in relation to distance from surface for a chromised low-carbon steel

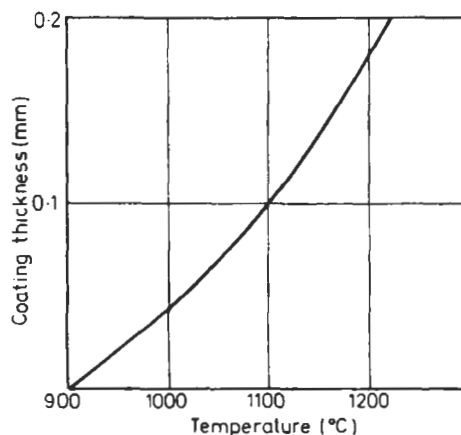


Fig. 12.21 Chromised low-carbon steel; coating thickness as a function of temperature; treatment for 4h

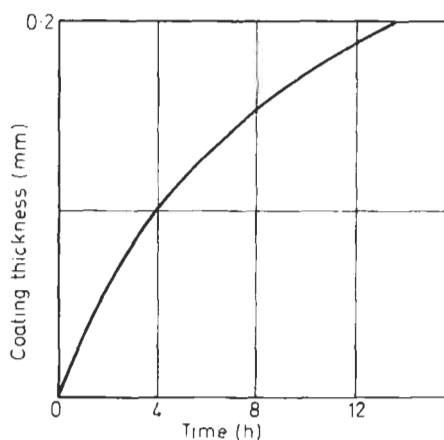


Fig. 12.22 Chromised low-carbon steel; coating thickness as a function of time; temperature 1 100°C

the effective coating thickness, the shallow transition zone to the right being ignored for practical purposes. If a chromised specimen is etched in nital, only the effective coating will remain unattacked. The core of such a specimen can be dissolved in boiling nitric acid, leaving the effective coating as a complete 'shell' which can be analysed. The average chromium content of a chromised coating on low-carbon steel is of the order of 25%. By comparing the overall chromium uptake with the weight increase of a complete specimen, it is possible to determine the relative contributions of interchange and reduction (or thermal dissociation) reactions during processing.

The influence of temperature on coating thickness is shown in Fig. 12.21 which relates to a 4 h treatment at temperature. Figure 12.22 shows the variations of thickness as a function of time at a constant temperature of 1 100°C. This curve is in good agreement with the third of Fick's equations (12.15):

$$x^2 = 4kDt$$

From such curves, taking $k = 1$, the values of D for different temperatures can easily be derived and an energy of activation for the process calculated. This has been found to be of the order of 239–247 kJ/mol^{4, 21, 24}. Increasing the carbon content of the steel progressively reduces both the rate of diffusion and the energy of activation²⁹.

Characteristics of Diffusion Coatings

The structure and composition of diffusion coatings depends of necessity on the metal or alloy from which the article is made. Thus, for example, it is not possible to speak of chromised coatings generally; the material into which chromium is diffused must be specified. Some data on methods of application and properties of commercially chromised irons and steels are given in Table 12.4.

Table 12.4 Diffusion coatings obtainable on ferrous materials

<i>Base material</i>	<i>Coating element</i>	<i>Processing temperature range (°C)</i>	<i>Method</i>	<i>Coating characteristics</i>
Iron Low-carbon steels Low-carbon alloy steels Decarburised malleable iron	Chromium	980–1 050	(Halide) 1. Gaseous 2. Semi-gaseous 3. Pack	25–75 μm Solid-solution (ferritic) 20–25% Cr Ductile (200–300 HV) Weldable Heat treatment acceptable *
	Zinc	350–400	Cementation (rotary furnace)	12–50 μm Single-phase intermetallic 90–95% Zn Fairly brittle Can be soldered and spot welded
	Aluminium	850–950	1. Cementation 2. (Halide) pack	125–750 μm Single-phase intermetallic Not exceeding 25% Al Brittle Not weldable
	Silicon	900–1 050	(Halide) 1. Gaseous 2. Semi-gaseous 3. Pack	125–250 μm Solid-solution (ferritic) Average 15% Si Brittle (160–180 HV) Not weldable
	Boron	800–1 050	(Halide) 1. Gaseous 2. Semi-gaseous 3. Pack 4. Salt-bath electrolysis	Up to 500 μm Matrix plus borides Brittle Hardness up to 1 500 HV Heat treatment acceptable *
Medium and high-carbon steels Cast irons	Chromium	850–980	(Halide) 1. Gaseous 2. Semi-gaseous 3. Pack	4–40 μm Matrix plus chromium carbides 60–80% Cr 1 500–1 800 HV Heat treatment acceptable *
	Zinc	350–400	Cementation (rotary furnace)	12–50 μm Single-phase intermetallic 80–90% Zn Brittle Spot-welding and soldering possible

Table 12.4 (*continued*)

<i>Base material</i>	<i>Coating element</i>	<i>Processing temperature range (°C)</i>	<i>Method</i>	<i>Coating characteristics</i>
	Aluminium	850–950	1. Cementation 2. (Halide) pack	50–350 μm Single-phase intermetallic Average 25% Al Brittle Not weldable
	Boron	800–1 050	(Halide) 1. Gaseous 2. Semi-gaseous 3. Pack 4. Salt-bath electrolysis	Up to 500 μm Matrix plus borides plus boron carbide Brittle Hardness up to 2 000 HV Heat treatment acceptable*

* The mechanical properties of the core material can be subsequently restored by suitable heat treatment.

Chromising of Iron and Low-carbon Steels

The coating is a chromium-iron alloy, showing a columnar ferrite grain pattern (Fig. 12.17*b*) and has most of the properties of a stainless chromium-iron. Carbides may be present in the coating depending on the carbon content of the steel and on the conditions of processing, and also nitrides^{30,31}. The carbides reduce coating ductility and corrosion resistance and so titanium-stabilised steels in which the carbon is 'fixed' as titanium carbide, have been developed; large quantities of such steel are now chromised as flat sheets and fabricated by pressing, e.g. to make heat exchanger shells.

Being of stable ferritic structure, the coating is not affected by heat treatment, and chromised articles can be normalised, air-hardened or quenched without detrimental effect to the coating. Spot-welding, arc or gas welding (preferably with 18 Cr–8 Ni-stabilised rods), and most methods of brazing and of silver soldering can be used on chromised low-carbon steel surfaces.

Chromising of Carbon Steels and Cast Irons

Carbon has a great affinity for chromium. When chromium diffuses into a steel containing appreciable amounts of carbon, the latter diffuses outwards and combines with the inward stream of chromium atoms to form a continuous carbide 'barrier' which effectively blocks any further diffusion in depth. Accordingly, when medium- or high-carbon steels are chromised the coating contains a high proportion of chromium carbides, and the average chromium content may be as high as 70–80%. There may be a layer of chromium-containing pearlite just beneath the coating and beneath this again a decarburised zone (carbon having diffused into the coating). Given sufficient time after the carbide barrier has formed, this zone may be recarburised from the core. Thus the final structure depends on the kinetics

of diffusion and carbide formation^{31,32}. The high hardness and low coefficient of friction of the chromised surface give it useful abrasion-resisting properties. The hardness of the coating is not affected by subsequent heat treatments which may be required in order to recover the mechanical characteristics of the core material.

Most tool and die alloy steels can be classified within this group. Care should always be exercised during processing to avoid a decarburised layer beneath the coating.

Most cast irons, except those fully decarburised during malleabilising, give coatings of the chromium carbide type. In view of the great variations in composition of cast irons, reproducibility of results can be achieved only by careful control of specification. High phosphorus and sulphur contents are detrimental to the formation of non-porous coatings.

Chromising of Alloy Steels

Apart from carbon, other elements present in commercial steels exert a great influence on the nature of the chromised coating. Generally speaking, austenite formers (manganese, nickel, cobalt, copper, etc.) have a retarding effect on the rate of diffusion. Chromised coatings on austenitic stainless steels may vary from relatively thin coatings of high chromium content to thicker coatings averaging 35% Cr³³, depending on such factors as carbon content and stabilisation and whether interchange (Cr with Fe, but not with Ni) or reduction reaction predominates. Maraging steels, because of their extremely low carbon content, chromise well and can be age-hardened afterwards. Ferrite formers (chromium, vanadium, aluminium) and strong carbide formers (molybdenum, tungsten, titanium, zirconium) tend to promote faster diffusion with smoother concentration gradients.

Chromising of Nickel, Cobalt and Alloys

Nickel and cobalt and their alloys lend themselves readily to chromising. The reaction is primarily one of reduction. The effective coating on pure nickel contains an average of 35–45% chromium and has good ductility. There is no sharp diffusion boundary as might be expected from consideration of the nickel-chromium constitution diagram, but an outer chromium-rich β -phase layer may be present, depending on the conditions of treatment, a sharp boundary and concentration gap separating this from the α -phase layer (Fig. 12.17c and d). A two-phase layer may develop at the boundary at certain rates of cooling⁷. The nickel-chromium surface alloy has useful oxidation- and thermal-corrosion-resisting properties.

This brief summary illustrates the fact that a wide range of coating properties can be obtained by applying the same type of processing treatment to different materials. Table 12.4 shows the types of coating obtainable on ferrous materials.

Aluminising of 'Superalloys'

Nickel- and cobalt-based high-temperature alloys are commonly protected

against high temperature corrosion by 'aluminide' coatings, generally applied by pack methods^{2,35}. For the stringent operating conditions of components such as gas turbine vanes, the aluminising process must be controlled to suit the particular alloy^{36,37}. The coating should consist of *high* melting aluminides of nickel or cobalt, modified by the presence of chromium and other constituents of the alloy; the aluminium rich aluminides of lower melting point are to be avoided. Thus the rate of aluminium uptake must be limited. The structure of the coatings is complex; carbides often form beneath the aluminide layer^{38,39}.

Chromium powder is often included in the aluminising mixture. Chromium and aluminium may diffuse together (*chromaluminising*⁴⁰) or by balancing the activities of chromium in the alloy and the pack, de-chromising may be prevented. Alloying of the chromium and aluminium powders⁴⁰ may be used to control aluminising.

Aluminising is also applied to stainless steels to increase oxidation resistance.

Properties of Diffusion Coatings

Some of the more important properties of diffusion coatings have already been mentioned. Generally speaking, the properties of a diffusion coating are those to be expected from a wrought or cast alloy of the same composition. Thus the corrosion-resisting properties of chromised low-carbon steels are very similar to those of a high-chromium stainless iron⁴, and sherardised materials behave much in the same way as galvanised steel or iron-zinc alloys. This generalisation of course assumes that the coatings are substantially non-porous. For example, the presence of carbon in steel may result in the formation of slightly imperfect chromised layers which are prone to develop pin-point corrosion in strong electrolyte corrodents such as sodium chloride, whereas the use of steels in which carbon is stabilised by a strong carbide-former such as titanium gives coatings of perfect continuity and structure, which provide adequate protection for all types of wet-corrosion conditions. Much of the value of modern techniques lies in the controlled production of homogeneous non-porous coatings.

It must always be remembered that diffusion coatings are produced by a form of heat treatment and that, with the exception of low-temperature zinc diffusion (sherardising), the treated ferrous materials are usually in the annealed condition. Whenever the mechanical properties of the parts must be restored to their original level, a subsequent heat treatment is necessary⁷. This does not as a rule present any difficulty with chromised or boronised steels. In order to prevent undue distortion and internal stresses during treatment and subsequent hardening, it is recommended that high-carbon and alloy steels should be processed in the 'normalised' condition.

Fig. 12.23 shows the variation of hardness with distance from surface for a chromised high-carbon steel (1% C). The full line represents the material 'as treated', the broken line corresponds to conditions after full-hardening and tempering. The apparent greater depth of the hard zone in the heat-treated material is due to the effect of small concentrations of chromium

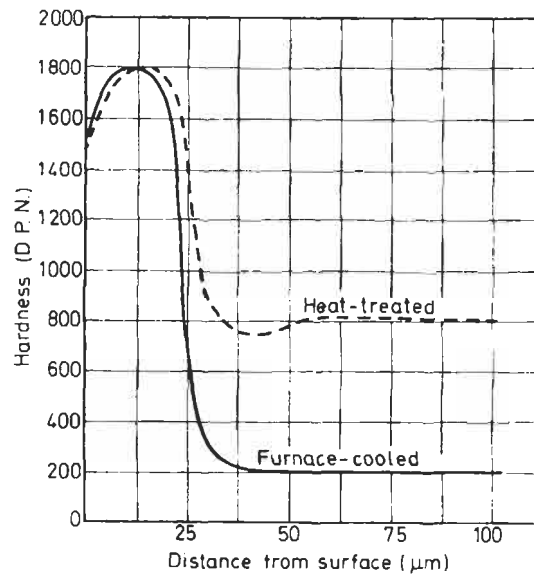


Fig. 12.23 Hardness as a function of distance from surface-chromised high-carbon steel (1% C)

immediately underneath the chromium carbide layer. With suitable processing conditions, the hardness may approach 2 000 HV and the drop at the surface is minimal.

Among the most important purposes for which diffusion coatings are applied are high-temperature-oxidation and thermal-corrosion resistance^{31, 41-43}. Their resistance behaviour in this context differs in some respects from that of plain alloy materials. The diffusion mechanism which is responsible for the formation of the protective coating will also take place whenever a treated part is reheated within the same range of temperature. This creates a gradual diffusion of the solute atoms in the parent metal without compensation for their reduced concentration at the surface, so that the nett result is an impoverishment of the alloy composition throughout the coating.

The practical implications of this 'rediffusion' effect are twofold. In the first place, the nominal composition of a diffusion coating may be such as to suggest by analogy with an alloy that it will have good oxidation resistance at a temperature of, say, 900°C. This is, however, true only if the rate of diffusion of the coating metal at that temperature is negligible or small enough to be compatible with the anticipated life of the component. The deep coatings (which generally presuppose a high rate of diffusion) are not necessarily the most suitable for high-temperature stability, and it is often preferable to utilise coatings where the diffusion process has been arrested by the formation of a diffusion 'barrier' (see above).

These features are well illustrated in the case of the chromising of ferrous materials. The weight increase of chromised low-carbon steel as a function of time at different temperatures is shown schematically in Fig. 12.24. At a temperature of 700°C, the weight increase in air is practically negligible, and

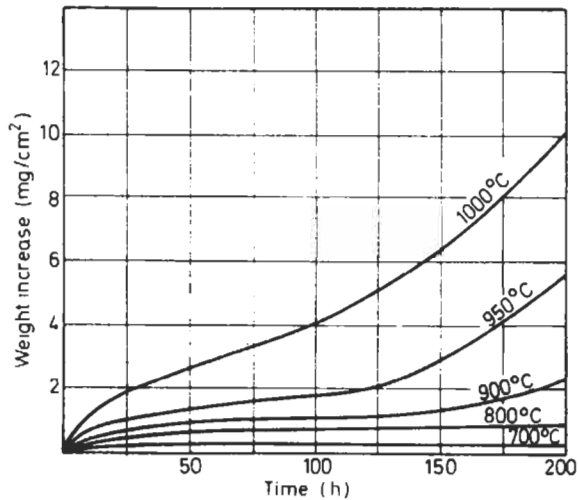


Fig. 12.24 Rate of oxidation of chromium-diffused mild steel (0.15% Cr) when heated in air at various temperatures

it is very small at 800°C, the curve showing the parabolic weight-increase/time relationship which is typical of good heat-resisting characteristics. When the temperature is raised to 900°C, the first part of the curve follows the normal parabolic pattern, but after some 100–150 h the rate of oxidation increases. This effect becomes more pronounced at higher temperatures, and at 1 000°C the oxidation rate after 25–100 h is appreciably higher than that of a 30% Cr ferritic steel. This gradual deterioration in oxidation resistance can also be followed by analysing the oxide scale at the surface. A thin, strongly adherent chromium oxide film is predominant at temperatures up to 900°C. At higher temperatures there is a gradual increase in the iron content of the superficial oxides which is due to continuous diffusion of chromium inwards and diffusion of iron towards the surface. In time, the composition will reach a level where the chromium concentration is too low to provide adequate oxidation resistance. It is of interest that for chromised *pure* iron, continued diffusion is much faster below 900°C (core ferritic) than at just above 900°C (core austenitic)⁴⁴. However, for chromised steel this effect is evidently off-set by the very low solubility of the thin carbide diffusion barrier in ferrite, as indicated by service life at elevated temperatures.

Table 12.5 Temperature range at which 'rediffusion' becomes appreciable

Coating metal	Basis metal	Temperature (°C)
Aluminium	Ferrous materials	700
	Nickel-base materials	950
Chromium	Low-carbon steel	870
	High-carbon steel	950
	Nickel-base materials	950

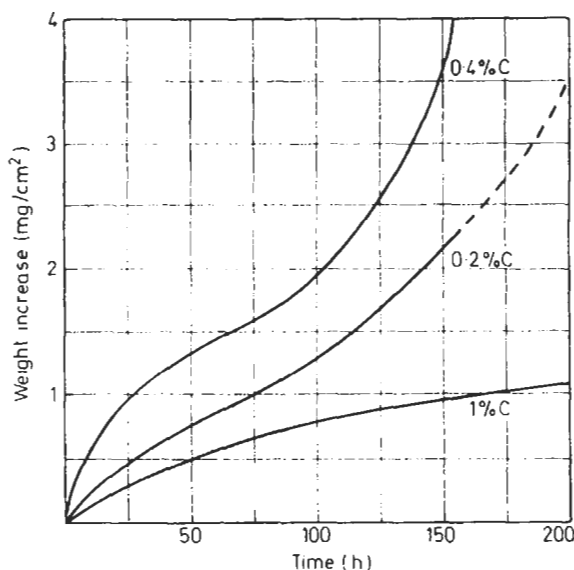


Fig. 12.25 Influence of carbon content on the rate of oxidation of chromium-diffused steel at 950°C

The temperature above which 'rediffusion' becomes important in service is shown in Table 12.5 for several systems.

The effect of coating, composition and of substrate structure on the oxidation rate is shown in Fig. 12.25 which gives weight-increase/time curves for oxidation in air at 950°C of three steels of different carbon contents.

The low-carbon steel (0.20% C) has a ferritic-type coating, and the core structure is primarily ferrite at temperatures below 880°C. After some 100 h exposure to oxidation the 'rediffusion' effect becomes appreciable, and the oxidation rate increases accordingly. In marked contrast, the high-carbon (1% C) steel has a primarily carbide-type diffusion coating which has good oxidation resistance. The low solubility of chromium carbide in austenite at 950°C stabilises the coating composition, which remains substantially unchanged for several hundred hours. At an intermediate carbon content (0.4% C), the coating is primarily ferritic but contains a certain percentage of carbides, mainly at the coating/core interface. Although the coating possesses good intrinsic resistance to oxidation and the carbide layer provides a diffusion barrier, the rate of oxidation is higher than for the low-carbon steel. In this case, failure is due to poor matching between coating and core structure, the ferrite-pearlite structure of the parent metal which develops on cooling introducing stresses in the coating. On reheating, these stresses cause cracks in the protective coating with consequent failure in a comparatively short time. The inherent stresses in chromised coatings³⁰ are not of great importance in practice.

In addition to providing coatings resistant to air oxidation, diffusion methods are of considerable value in reducing the detrimental effects of sulphur corrosion at high temperatures. Both aluminised and chromised coatings are also used for protection against lead-corrosion and in preventing

intergranular oxidation of steels and nickel-base alloys in certain atmospheres.

Recent investigations in the diffusion coating field have added little to the principles involved. However there have been some detailed studies and practical developments examples of which are noted below. 'Diffusion coatings' are now often classified with 'chemical vapour deposition' processes. For example, the three-part review of diffusion coatings by Sequeira *et al.*⁴⁹ is very useful and the hard carbide coatings formed by pack-chromising high-carbon steels are identical with those formed by CVD, with equally good corrosion resistance^{50,51}.

Mukherjee⁵² studied the gas phase equilibria and the kinetics of the possible chemical reactions in the pack-chromising of iron by the iodide process. One conclusion was that iodine-etching of the iron preceded chromising; also, not unexpectedly, the initial rate of chromising was controlled by transport of chromium iodide. Neiri and Vandenbulcke⁵³ calculated, for the Al-Ni-Cr-Fe system, the partial pressures of chlorides and mixed chlorides in equilibrium with various alloys and phases, and so developed for pack aluminising a model of gaseous transport, solid-state transport, and equilibria at interfaces.

Microprobe studies of pack-chromised iron (Cr powder, alumina, CrCl₃ mixture) shows that the surface Cr concentration builds up with time to 95% in 20 h at 1300 K⁵⁴, and that the diffusion coefficient for Cr in α -phase is very concentration dependent. The growth of carbides during pack-chromising^{51,55,56} and during gas-vanadising⁵⁷ have been studied.

The control of carbon diffusion is important when steels are chromised (see 'Chromising of Iron and Low-carbon Steels' *et seq.* above). The problem of decarburisation is particularly important for high-carbon steel components of thin sections. Decarburisation can be reduced by addition of titanium to the chromising 'pack'⁵⁸; presumably early formation of titanium carbide prevents loss of carbon to the 'pack' before a stable carbide barrier is formed. It is claimed⁵⁹ that nitriding (without nitride formation) prior to (gas) chromising slows carbon diffusion by promoting austenite formation, produces a single-phase carbide, and so reduces surface cracking, a problem with chromised medium-carbon steels.

Aluminide coatings for gas turbine blades continue to receive much attention. The patent literature contains numerous modifications, for example diffusion of Hf⁶⁰ or Y⁶¹ during pack aluminising, or preliminary plating with Pt-group metals, to increase resistance to thermal corrosion. A preliminary coating with nickel can form a barrier to carbon diffusion⁶². Wing and McGill⁶³ have reviewed the Pt-aluminide coating, and Vogel *et al.*⁶⁴ have studied brittle-ductile transition. During aluminising, the aluminium diffuses through the platinum which is found in the surface layer as PtAl₂. Another example is the silicon-aluminide coating of Young and Deadmore⁶⁵, an example of the slurry or paste technique. Goward and Cannon⁶⁶ have reviewed pack-cementation coatings for superalloys.

Other diffusion coatings include manganising⁶⁷ to produce austenitic or martensitic surface layers on steel. Mixed Mn/Cr diffusion coatings are readily produced by pack techniques. Carbide coatings based on Ti, V and Cr, singly or in combination, are mainly produced for their wear-resisting properties⁶⁸. There are now several commercial boronising processes⁶⁹. Con-

trol of the processing to produce single-phase Fe_2B coatings is recommended. Boron may be co-diffused with Cr, V, Ti etc.⁷⁰

Finally, some alternative processing techniques should be mentioned. Aluminothermic mixtures for pack chromising etc. are based on the coating metal as oxide, aluminium, alumina and a halide; the aluminium reduces the oxide during processing, generating useful additional heat. Some aluminium may be taken up by the steel. Kaluna and Wachowiak⁷¹ have described the aluminothermic chromising of 0.5% carbon steel and illustrated the coating structures.

The 'Dilex Process' utilises a molten lead bath⁷² as transfer medium and is applicable to diffusion coatings of Cr, Al, Ti, Mo, Ni and Co. Finally, a Japanese fused borate bath process⁷³ produces carbide coatings (Cr, V, Nb or Ta) on carbon and tool steels. The coatings are wear and corrosion resistant. The 'TD Process' uses this technique.

The present treatment has been limited to a general survey of diffusion coatings; for a more complete account on specific aspects, the reader should consult the references.

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12.4 Principles of Applying Coatings by Metal Spraying

The metal spraying process originated in the work of the late Dr. M. U. Schoop of Zurich, who took out the original world patents for it, between the years 1910 and 1913. The idea was then so revolutionary that many exaggerated claims were made for the coatings produced, with the result that it was a long time before the method really made commercial headway. The first experimental practical use of the process was made in France and Germany during World War I, but commercial development on a considerable scale only took place in England in the early 1920s. Great use was made of the process during World War II and expansion has continued in most countries ever since. At reasonable intervals the method forms the topic of international conferences.

Methods of Spraying

Four main methods are used in metal spraying, the variation being in the initial form in which the metal is used. The earliest process employs molten metal. The metal is poured into a container and is allowed to flow through a small nozzle surrounded by an annular orifice, through which compressed air or other compressed gas is fed. The stream of molten metal is divided into small particles, as in a scent spray, and as the gas pressure used is high, each particle travels forward at a high velocity. If the droplet strikes a suitable surface while in the molten condition, it will adhere and form one member of a deposit. The process, originally employed in the UK for zinc spraying steel window frames, finds a limited outlet in the repair of dents in motorcar panels and for the backing of metallic rectifiers with fusible alloys. The disadvantages of the process are: (a) the tools are rather awkward to handle as they contain molten metal, (b) the metal must be easily fusible and (c) there is a good deal of erosion on the nozzle orifice. Among the advantages of the method are cheapness, as the metal used has not to be processed in preparation for its use in spraying in any way and the heat is usually obtained from town gas at normal pressure and oxygen is not required.

The second process (the Schori process)* of metal spraying is that in which

*F. W. Berk Ltd. (Engineering Division), London, W5.

metallic powders are used as the raw material and are mixed with a stream of gas, which may be air or a combustible gas. This stream is fed into a central nozzle, again surrounded by an annular orifice. The annular orifice is fed with a fuel-gas and oxygen mixture which would normally give a blow-pipe flame on ignition, and the passage of the powder through the flame results in the melting of most of the particles. Compressed air or other gas is fed through a second annular orifice surrounding the gas ports, with the result that the molten powder particles are projected forward as in the molten metal process.

With modern methods of powder production it has become possible to increase the output and efficiency of powder pistols by introducing the powder, not through a central duct in the nozzle, but through four or more small ports interspaced with a similar number of gas ducts in a ring formation. The nozzle bearing this multiplicity of ducts is surrounded by an outer case forming an annular space through which the propellant gas (usually air) flows. The tools are fed from a specially designed powder container fed by positive pressure, and outputs of 50 kg/h are not unusual.

The advantages of the modern form of this method are that many alloys that cannot be conveniently drawn into wire form can be used in the process, that the hand tool contains no moving parts, and that high outputs can be obtained. The disadvantage of the powder system is that it is not very suitable for high-melting-point metals, and the losses are higher than with wire, because not all the particles are melted.

The third and most highly developed method uses a metal wire as the raw material. The wire is fed into the central orifice of a nozzle resembling that of the powder pistol; it passes through an intense oxy-gas flame and is sprayed by an air blast provided by the feed of air into an orifice surrounding the gas ports. In the case of hand pistols, the wire is fed by a mechanism in the tool itself, powered by compressed air which is fed through the same supply that provides air to the nozzle. The feed of the wire can be synchronised exactly with the rate of melting. This process will deal with all metals that can be drawn into wire, and which can be melted in any oxy-gas flame. As all the metal sprayed must first be melted, there is much less loss with this process than with the others. The tools weigh from 1.4 to 1.8 kg and can be handled without difficulty. The disadvantage of this process is that it is applicable only to metals ductile enough to be produced in wire form. It is essential that the feeding mechanism in the pistol is kept in good order. Some modern pistols also have automatic governors incorporated so that the wire speed remains constant.

The demand for higher output and greater efficiency has been met by a steady improvement in the design of wire pistols. The small high-speed turbine and its attendant reduction gear is now often replaced by a special air-driven displacement motor giving a more positive drive to the wire. The group of valves controlling the gaseous feeds have been modified to give positive action and freedom from leaks. While the nozzle design is basically similar, improvements in wire quality and accuracy of nozzle part manufacture allow outputs from the hand tools similar to those from the powder gun and comparable to those from early mechanised tools. Wire pistols need three gas feeds:

1. A fuel gas under pressure which may be hydrogen, towns gas, acetylene or propane. With special nozzles, low-pressure acetylene or butane can be used, but it is not common practice. The use of single cylinders of fuel gas is now giving way (except under site conditions) to the gases drawn from bulk liquid storage. All modern installations use flow-meters in the gaseous feeds.
2. Oxygen from cylinders or bulk storage for the tools.
3. Compressed air at pressures of from 4 to $6 \times 10^2 \text{ kN/m}^2$. The air supply must be free from suspended moisture and also be reasonably dry.

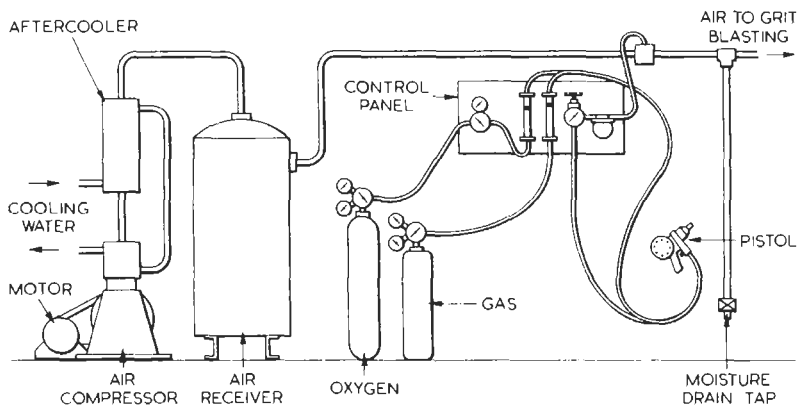


Fig. 12.26 Diagrammatic arrangement of compressed air and hoses for wire pistols

The general arrangement of the apparatus is shown in Fig. 12.26. In recent years both the powder and wire processes have been automated for large projects. Mechanisation allows the use of large nozzles of special contours and the replacement of pneumatic drives by electric motors. Controls are usually from consoles by pneumatic or electronic signal systems.

Improvements of the manual pistols have made it possible to use a much thicker wire which can be up to 8 mm dia for the softer metals. Recently, the range of the wire pistol has been extended by the spraying of plastic cords containing the material to be sprayed as a fine powder. This development, as yet, is not much used in the anticorrosives field.

Although at the time of his early inventions Dr. Schoop envisaged that an electric arc could be used to produce the molten metal for spraying, forty years passed before the method became commercially important. Then, in Germany, Russia and Japan tools were made based on the arc. Although in Japan alternating current is used, the noise is nearly intolerable and elsewhere direct current from motor generators is employed. The fundamental idea is simple; two wires, carefully insulated from each other, are advanced to meet at a point where an arc is formed, immediately in advance of a jet

of compressed gas, usually air. The metal melted by the arc is immediately broken down into a spray of fine droplets which are projected onto the work surface. In the UK the process had a limited use for spraying metals of high melting point for reclamation, but when metallic rectifiers and step-down transformers became common the future of arc spraying was assured. A transformer taking 3-phase current and delivering single phase to a rectifier giving out a direct current of up to 600 A at around 27 V is ideal for a spraying tool, and together with the controls can be a convenient size for workshop use. In general, arc deposits tend to be a little coarser than those from the best gas pistol, but because of the high temperature there is some incipient welding to the work face and adhesion is high. Unfortunately, as yet, spraying losses are higher than with the gas gun and the arc does not seem to have economic advantages over flame guns for the production of zinc coatings. There is a rapidly expanding demand for the system for aluminium, and by using wires of two metals, for coatings of mixed metals. The diameter of the wire used in arc pistols is normally about 1.6 mm and outputs of 8 kg/h are possible with aluminium.

Metals which are subject to oxidation or attack by nitrogen can be sprayed in a closed system so that air is excluded. The heat necessary to melt the wire is produced by current generated in the wire itself by high-frequency currents flowing in small water-cooled coils. By this means, titanium, niobium and even uranium, can be sprayed without gaseous contamination.

Before leaving this brief consideration of spraying methods it should be noted that metal can be deposited by plasma or constricted arc and by detonation. In the plasma process an arc is struck between a central electrode of a refractory metal such as tungsten and the rim of a water cooled nozzle, often of copper. The nozzle forms a small chamber in which the arc is constricted by the pressure of the spraying gas. This is one of the inert gases such as argon, helium or mixtures of these with nitrogen. The temperature of the arc plasma can greatly exceed 5 500°C and the material to be sprayed is introduced into the nozzle chamber as a fine powder of diameter in the range of 5–40 μm .

While plasma deposits are widely used, especially in the American aero industry to provide wear resistance, there is not at the moment any great demand for the exotic materials deposited to be used as a protection against corrosion. However, M. A. Leinstein of General Electric (USA) reports the successful use of sprayed chromium carbide as a protection for ventilator blades operating in corrosive conditions.

Finally, it should be noted that there is now a method of coating by detonation which in some ways is akin to spraying. Briefly, mixtures of explosive gases charged with the coating material as a fine powder are fired in a special strong tubular chamber with a small exit. At each explosion the powder leaving the exit strikes the work face at high velocity. After each detonation (many times per minute) the chamber is swept clean with nitrogen. As yet the demand for these deposits is for wear resistance but they could be important as a protection against high temperatures. Unlike most spraying processes, the apparatus is not mobile and the operation is carried out in sound-insulated chambers. In some cases when plasma deposits fail detonation may provide an answer.

Surface Preparation

As with all metal coating processes, the success of the finished deposit depends considerably on the surface to which it is applied. Most metal coating processes depend upon interatomic forces or alloy formation for adhesion; in metal spraying, on the other hand, the bond is entirely mechanical. Although each small particle arriving at the surface is molten, there is not sufficient heat present to produce incipient welding to the surface and the process is virtually cold. Adhesion is thus normally the result of a mechanical interlocking of metal particles with a clean and rough surface.

A suitable surface for the reception of ordinary metal-sprayed coatings as used for protection is obtained by blasting with angular grit, but not by shot blasting. When spraying is carried out in a works the normal abrasive used is chilled iron grit (BS 2451) Grade 2. On site, or where recirculation of abrasive is not easy, an aluminous grit (24 mesh) or some type of hard copper slag is used. Blasting with iron grit can be performed by means of compressed air or by airless blasting, in which case the abrasive is thrown by centrifugal force from the periphery of fast rotating wheels. This process is not suitable for the lighter abrasives. It goes without saying, that the function of the blasting is not only to give the required angular roughness but to ensure that the work surface is clean and free from all scale.

In cases where very high adherence is necessary an undercoating of sprayed molybdenum is applied. Owing to the volatile nature of its oxide this metal presents a clean surface to the workface and with most metals (except copper) very high adhesion is obtained. To a limited extent arc-sprayed aluminium bronze will also form a strongly adherent base coating.

Deposition by metal spraying can also be used for the reclamation of worn parts; in this case, surface preparation is often accomplished by machining, i.e. by cutting a rough thread on the surface or by increasing the surface area of the part by grooving. Such methods are not, however, normally used in corrosion prevention, except in the case of pump rods, which can be built up with nickel or stainless steel.

Sprayed Metal Coatings

Aluminium- and Zinc-sprayed Coatings

The metals most used for corrosion protection by metal spraying are aluminium and zinc, both of which are anodic to steel in most environments. Physical properties of these coatings are shown in Table 12.6.

Metal spraying is, however, capable of producing deposits of nearly all the metals and alloys of commerce. The great advantage which the process possesses over almost any other is that zinc and aluminium coatings can be applied to very large structures, such as bridge members. Usually these are treated in unit form, and after erection the coating is touched up on site. Examples of well-known structures that are zinc sprayed are the bridges over the Menai Straits and the Volta river in Africa, and the Forth and Severn

Table 12.6 Physical properties of sprayed zinc and sprayed aluminium

Material	Property				
	Density (g/cm ³)	Coating weight (kg/m ²) 0.025 mm thickness	Brinell hardness	Ratio of contraction stresses in sprayed deposits 0.51 mm thick	Compressive strength (stress to collapse) (MN/m ²)
Sprayed zinc	6.35	0.159	20-28	1	159
Sprayed aluminium	2.35	0.059	25-35	4	185

suspension bridges. The structure of the British Steel Corporation's mills at Margam, Trostre and Velindre in South Wales are sprayed with aluminium. Sprayed deposits of zinc and aluminium have protective properties proportional to their thickness. They have the advantage that, being of a matt finish, they absorb paint well.

The coatings produced by metal spraying have an unusual structure which is characteristic of the method of formation. They are composed of small particles usually not more than 0.01 mm in diameter which, having reached the surface in the molten condition, have splashed outwards and then solidified. Figure 12.27 (left) shows in section the irregular form of the flattened particles. In transverse section the surface profile is undulating (Fig. 12.27 (right)).

In all metal spraying processes the particles emerge from the nozzle in a conical stream, and although the particles near the centre are molten, those at the periphery have solidified. In the powder process there are in addition solid particles which have not melted. The solid particles tend to become entrapped in the coating, making it porous. The effect is more pronounced in the powder process owing to the larger number of solid particles present.

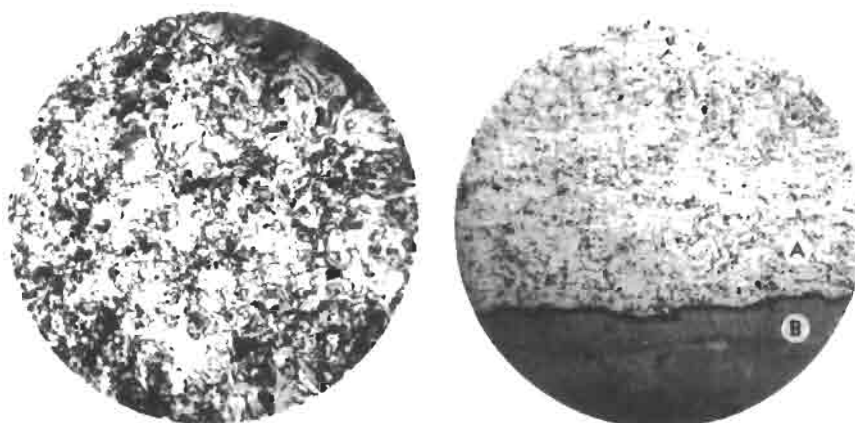


Fig. 12.27 Sprayed aluminium on steel. *Left*: section taken parallel to substrate and etched, $\times 75$. *Right*: section taken transverse to substrate and etched in HF, $\times 75$; A aluminium and B steel



Fig. 12.28 Transverse section of sprayed 0.4% C steel, unetched and $\times 75$

In the case of the reactive metals like aluminium and zinc, the particles themselves become coated with a thin oxide skin, so that the finished deposit contains very thin layers of oxide. In the early days it was thought that the presence of pores and oxide layers (Fig. 12.28) would cause trouble, but this has been found to be untrue, at least for anodic metals. In a zinc coating, in fact, pores should have little effect. Zinc protects by sacrificial action, and immediately an electrolyte permeates a zinc coating, corrosion will commence, giving rise to relatively insoluble products which will seal the pores automatically. Therefore if the zinc coating has sufficient weight per unit area, it will give complete protection. The life of a zinc coating applied by metal spraying, weight for weight, is equal to the life of a zinc coating applied by any other method.

Pores play an important part in the protective value of sprayed aluminium. Its behaviour when sprayed is entirely different from what would be expected from the massive metal. Sprayed aluminium is in fact used to protect wrought aluminium from corrosion. Aluminium coatings are slightly more porous than zinc coatings, and the interconnected porosity may be as high as 10%, although it is usually nearer 5%. Each particle of aluminium on the coating is surrounded by a very thin oxide layer. This layer is, however, discontinuous in places, so that the electrical conductivity of sprayed aluminium coating is quite high.

From its position in the electrochemical series, aluminium would be expected to protect steel at discontinuities more effectively and over a wider area than zinc. Aluminium with an oxide film is, however, more noble than zinc, and thus although sprayed aluminium will protect steel by sacrificial action, its action in this respect is not so marked as that of zinc. Thus an electrolyte passing through a sprayed aluminium coating in the first few hours of its life will cause corrosion, with the formation of very insoluble substances, which completely seal the pores of the aluminium, so that after a little time the aluminium coating becomes absolutely impervious to moisture. In the event of mechanical damage this self-healing mechanism is supplemented by sacrificial action, insoluble products form and a scratch is healed almost immediately. Aluminium does not give heavy corrosion products and therefore coatings of paint on the sprayed layer do not tend to lift.

Aluminium-sprayed coatings on steel have been exposed for over 20 years in very severe atmospheric conditions (such as those at Congella near Durban) and have given perfect protection; the only result of long exposure has been the appearance of a few small nodules of aluminium oxide which appear to have little or no significance as sites of future corrosion.

Aluminium coatings are extremely attractive from the point of view of protection in both immersed and atmospheric conditions, but they are most advantageous when the electrolyte of the corrosive medium is of high conductivity. While aluminium-sprayed coatings give good results in sea water, and excellent results in sulphurous atmospheres, a combination of sulphur and chlorine seems to reduce the insolubility of the corrosion product, and for resistance to such combined attack zinc is preferable to aluminium. If a freshly sprayed aluminium coating on steel is exposed to pure water for a few hours it sometimes becomes covered with a brown stain. This is due to the aluminium acting cathodically to the steel during the first few hours. The action appears to be due to the oxide layers. A very small quantity of iron is corroded during the initial period, but after a little time the aluminium acts normally as anode. The insoluble aluminium oxides formed are coloured by a small amount of iron, and it has been proved that these brown stains, although unsightly, do not have a significant effect on the expectation of life of the aluminium coating.

The thicknesses of the deposits are normally those recommended in BS 2569, Part 1*, i.e. 0.01 mm (0.004 in) in the case of aluminium and 0.075 mm (0.003 in) for zinc. If the surface is to be subsequently painted, the thickness is sometimes reduced to 0.05 mm (0.002 in). It should be realised that these thicknesses are the average, the high and low spots varying 0.025 mm (0.001 in) up and down. For immersed conditions some specifications call for 0.2 mm (0.008 in) coatings of aluminium. Recently, it has been shown that layer corrosion in high-tensile aluminium members is completely prevented by spraying with aluminium, and it is worthy of note that the best results for this purpose and for the protection of steel are obtained with an aluminium of commercial purity, containing 99.5% of aluminium (the main impurity should not be of copper). Commercial aluminium of this purity is much more effective than the 'super-pure' metal. It is now suggested that aluminium-zinc alloys containing from 25 to 95% Zn give better protection in certain conditions than either of the components alone. There appears to be some evidence that this is the case in stagnant sea water, but much more practical experience will be necessary before these alloys can be generally recommended. The raw materials would be available in powder or wire form, but it is probable that, although there is no difficulty in the actual spraying process, the cost would be greater.

An interesting application of sprayed aluminium is for resistance to high-temperature oxidation up to 900°C. The article is grit-blasted and aluminium sprayed, usually to a thickness of 0.008 in (0.2 mm). It is then treated with a sealing composition which may be bitumen or water-glass, and is diffusion annealed in a furnace at 850°C for approximately 30 min. The final coating

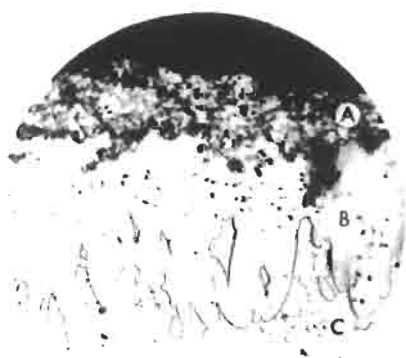


Fig. 12.29 Aluminised steel. *A* Al_2O_3 + aluminium, *B* Fe-Al alloys and *C* steel; $\times 75$

consists of a gradation of aluminium-iron alloys with a skin of aluminium oxide (Fig. 12.29). Such deposits will withstand oxidation for very long periods at temperatures up to 900°C . Above this temperature the diffusion of iron into the aluminium becomes so rapid that the alloy layer becomes impoverished and the upper layer contains insufficient aluminium to provide further protection. Deeper penetration is obtained using this method. The process can be used on some cast irons, but if the free graphite content is too high the aluminium layer will not prevent growth.

Lead Sprayed Coatings

Lead is a toxic metal and rigid precautions against lead poisoning are essential. Sprayed lead is, like other sprayed metals, porous, and the sprayed layers will not as a rule withstand attack by strong acids. On the other hand, lead from 0.13 to 0.25 mm (0.005 to 0.01 in) in thickness has proved extremely useful in atmospheres containing sulphuric acid. In this case the pores in the lead become blocked with lead sulphate, with the result that complete protection is assured. In the event of mechanical breakdown, lead does not exhibit any sacrificial action and therefore corrosion may lift the lead layer.

Tin Sprayed Coatings

Tin can be sprayed by all the processes mentioned above, and is very often used for food vessels. The advantage of the spraying process is that heavy layers of pure tin can be deposited. As the layer is porous, it is usual to apply 0.38 mm (0.015 in) and polish the deposit. The polishing of tin, which is a soft metal, completely seals the pores. When tin coatings have to be used in deep-freeze conditions, there is a likelihood that pure tin will be transformed to a grey powder, owing to allotropic change. This is completely prevented by using tin containing 0.75% of bismuth, and this alloy can readily be used in the metal spraying process.

Copper Sprayed Coatings

Copper and its alloys are all cathodic to steel, therefore sprayed coatings of these materials are not used for protection, except for ornamentation work in the interior of buildings, or in conditions such as where there is a minimum humidity.

Stainless Steel, etc.

Most stainless steels can be sprayed, but it is necessary to use material which has been stabilised against weld decay, because during spraying the stainless steel particles pass through the critical temperature range. Stainless steel coatings are porous, hence, it is not economical to spray tanks with these alloys, as it would be necessary to polish the surface to ensure that no discontinuities were present. Pump rods, shafts and rolls are now reclaimed and resurfaced with really heavy deposits of several millimetres in thickness which are afterwards ground and polished. Under these conditions stainless steel gives good service. The above remarks apply, in addition, to coatings of nickel and Monel. These coatings give good results on rods where a ground and final high finish is possible.

For resistance to high-temperature oxidation in air, at temperatures above 900°C, good protection may be obtained by spraying nickel-chromium alloys and then heat treating at 1 100°C so that diffusion takes place. Such coatings are extremely useful under high-temperature conditions where it is not economical to use solid nickel-chromium alloys. Under some furnace conditions, solid nickel-chromium parts sometimes give unsatisfactory results owing to attack by sulphurous gases. This can be largely overcome by spraying them with aluminium.

Mechanical Properties of Sprayed Metal Coatings

The strength and adhesion of sprayed metal coatings are extremely difficult to measure with precision, and the properties of sprayed metals vary greatly with the spraying conditions and with the conditions of test. It is difficult, therefore, to correlate the values taken from the literature on the subject. For instance, American workers produce tensile test pieces by depositing on to 9.5 mm (0.375 in) steel tube and then machining out the tube. By this method the results shown in Table 12.7 were obtained.

On the other hand, the ultimate strength obtained by testing solid sprayed bodies in the UK gives values about one-third of those in Table 12.7. The density of sprayed metal is between 10 and 15% lower than that of the wrought metal.

Spraying conditions make hardness values so variable that unless they are accurately known no comparisons are possible. Brinell hardness figures for sprayed molybdenum vary from 350 when produced with a reducing flame to 725 with an oxidising flame, and while a thick sprayed deposit of 0.8% carbon steel can give a figure of 330, the hardness of a particle obtained by micro hardness methods will be about 550.

Table 12.7 Mechanical properties of sprayed metals

<i>Metal or alloy</i>	<i>Ultimate tensile strength (MN/m²)</i>	<i>Elongation (%)</i>
Fe-18Cr-8Ni	206	0.27
Fe-13Cr	274	0.50
0.1% carbon steel	205	0.30
0.25% carbon steel	239	0.46
0.80% carbon steel	188	0.42
Aluminium	134	0.23
Bronze	139	0.45
Zinc	90	1.43
Molybdenum	51	0.30

Table 12.8 Hardness values (Brinell) for solid blocks of sprayed metal

<i>Metal</i>	<i>Hardness value (HB)</i>
Zinc	21
Aluminium	18
Copper	93
Monel	192
Mild steel	320
Fe-18Cr-8Ni	301
0.75% carbon steel	336 (kept cold during spraying)
0.75% carbon steel	280 (allowed to get the hot during spraying)

Hardness values ascertained for solid blocks of sprayed metal are given in Table 12.8. Values obtained in America on deposits 0.76 mm in thickness were about two-thirds of those given in this table. Figures for shrinkage of various deposits are given in Table 12.9.

Thermal conductivity can be as low as one-eighth that of solid metal; in the case of steel 7 W/m°C. The electrical resistance (specific) of copper, zinc and silver is about twice that of the cast metal, and of aluminium as much as five times, depending on spraying conditions. Adhesion in tension should

Table 12.9 Shrinkage of sprayed metal deposits

<i>Metal</i>	<i>Shrinkage (mm/mm)</i>
Fe-18Cr-8Ni	0.012
Fe-13Cr	0.0018
Ni + Cr + Mo steel	0.002
0.10% carbon steel	0.008
0.25% carbon steel	0.006
0.80% carbon steel	0.0014
Aluminium	0.0068
Bronze	0.006
Zinc	0.010
Molybdenum	0.003

be from 7.7 to 35 MN/m², but shear can be five times this according to the method of preparation.

For 30 years, large constructional engineering projects have been sprayed with zinc and with aluminium. Spraying has been done in metal spraying works, and no preferential treatment after transport to the site has been given. Experience has shown that the amount of touching up and repair of coatings on site necessary is extremely small. One can assume that if the grit-blasting process has been carried out satisfactorily the adhesion will be sufficient for all normal anti-corrosive work. It should be realised that the spraying process is essentially the casting of a great number of small particles under pressure, and the coatings have a strength comparable to that of a cast metal of similar thickness. It is clear that thin sprayed metal coatings cannot be expected to withstand rubbing friction or heavy mechanical damage. If coatings are applied to sharp edges some breakdown is to be expected. In constructional engineering most edges are radiused, and the problems connected with the corners do not arise. The spraying process can be applied wherever a pistol can reach the surface, and in order to extend its adaptability special nozzles which deflect the spray in angular directions are used. Straight tubes up to 2.5 m in length can often be sprayed internally by the wire process, by use of special nozzles, provided their internal diameter exceeds 32 mm.

Painting of Sprayed Coatings

While zinc sprayed coatings give excellent protection in themselves to steel, the matt surface is very reactive and hence becomes unsightly due to the formation of corrosion products. Galvanised steel gives a smooth surface and is therefore not an ideal base for painting and it is normal to use an etch primer to give the necessary adhesion. The etch primer is usually based on a butyral resin and free phosphoric acid, and it leaves the zinc surface with a thin inhibitive film. It is obvious that there is no need to etch a sprayed surface, and the late Dr. Jordan of the Paint Research Association suggested reduction of the free phosphoric acid by a quarter to 3.5–4%. This primer is now normally applied to zinc sprayed material before it leaves the metalising site. There is still no definite ruling as to the ideal paint system to follow the priming wash, but research on this is still being pursued at the Paint Research Station and elsewhere. Most paint systems give good results over sprayed zinc but certain oily media which react with the metal should be avoided. The use of inhibitors such as chromates has been found to be good in practice, but the less soluble zinc tetroxychromate is preferable to zinc potassium chromate. After much thought and in order to make the system used on the Forth and Severn bridges near-perfect, an undercoat of zinc tetroxychromate in a phenolic vehicle, followed by two coats of micaceous iron ore in a similar vehicle, were used. Very promising results have been obtained with the inert paints based on polyurethanes and vinyl copolymers.

The texture and drying properties of the paint are important. If it is too thin it will leave the peaks of the matt coating uncovered and if too thick, gas will be trapped in the valleys giving a tendency to blister. In view of the

success of the silicate-bonded zinc-dust paints, tests are now being made on paints with a silicate vehicle, usually ethyl silicate. All over the world, painted sprayed zinc has given good results in many types of exposure conditions and with many types of paint, and it is because of the need to produce the best paint that speculation and research continues.

Aluminium coatings exposed as sprayed show remarkable protective properties and in many cases the only evidence of age is the appearance of small hard nodules of aluminium oxide, and these do not appear to be deleterious. However, the dead white of the sprayed surface soon becomes discoloured by dirt and so a paint covering is usual. A chromate inhibitor is not essential and two coats of a simple vinyl-based sealing paint have given remarkable results in the tests of the American Welding Society over periods of 12 and 15 years.

Thin zinc sprayed deposits of 0.05 mm in thickness are used as a base for stove enamelled finishes on such structures as radar cabinets.

It is necessary to choose the type of paint with care. If it skins-over too quickly in the oven the gases cannot escape and blistering results, but if setting is deferred for too long the paint will flow to the base of the article. Some experimentation is advisable and the conditions once established should be retained. Some users treat the sprayed coating with a passivator of 200 g sodium dichromate in 1 litre of 6% sulphuric acid and dry it before enamelling.

Recent Developments

In recent years, the spraying process has been adapted for hard facing, using the chromium-nickel-boron alloys which have become known as Colmonoy. More recently still, the cobalt-base Stellite alloys have also been used. These materials in powder form are sprayed on to the surface in the usual way. The deposit is afterwards heat treated by a torch, so that fusion takes place. The process is often known as *spray-welding*. Such coatings are primarily used for hard facing under wear conditions, but as the final surface is nickel-chromium or cobalt-chromium they exhibit very high anticorrosive properties.

The spraying process provides a method of treating steel with coatings of zinc or aluminium, which can afterwards be painted. A combination of such a metallic primer and a good paint system is the most effective means of combatting corrosion of constructional steelwork at a reasonable cost that is yet known.

Addendum

The vision of the late W E Ballard ensured that this chapter is still very relevant but there have been some changes in emphasis. Of the spraying techniques, the electric arc process is now generally more economical in operation than oxy-fuel gas processes. The rate of spraying is proportional to the current used and several types of equipment are available ranging from 200 to 1 000 A capacity. For manual operation, pistols using currents up to

400 A capable of spraying, for example about 30 kg/h zinc are typical; equipment giving throughputs of 50 kg/h is used mainly for automatic spraying. Electric arc tends to facilitate the *achievement of* good adhesion, a point which has been particularly beneficial with aluminium, but which is of less significance with zinc which has adequate adhesion using either source of heat.

Adhesion is mechanical. For anti-corrosion protection by zinc or aluminium, an adhesion value of about 3 MN/m^2 is sufficient; 7 MN/m^2 is typical and more than 15 MN/m^2 can be obtained. There is no alloying to the substrate as the temperature of the sprayed metal is quite low when it reaches the steel surface (this can be demonstrated by spraying onto glass which does not crack with the limited heat received).

Coatings up to more than $500 \mu\text{m}$ ($3\,200 \text{ g/m}^2$ zinc) can be applied to suit requirements, but with aluminium it is usually best to spray $100\text{--}200 \mu\text{m}$; more than $200 \mu\text{m}$ is unnecessary. In manual spraying, the uniformity of the coating depends on the skill of the operative. Spraying in horizontal overlapping lines gives more uniform thickness than the 'cross-hatch' technique.

The importance of inspection must be stressed. Work should be inspected at four stages: (1) prior to treatment; (2) after surface preparation and immediately before spraying; (3) after spraying; and (4) after storage or transport. If delay occurs in the inspection prior to spraying, or after spraying and prior to painting, extra costs are involved in re-preparing the surface. Clients who quite reasonably insist on inspection at these stages should therefore also insist that their inspectors are available promptly of the required time.

Where the end use of the product is known, there is usually preference to use either zinc or aluminium, both technically and because of the works problems associated with use of an alloy (identification, separation of overspray). However, in some countries (such as the United States) where there has been a recent surge in anti-corrosion uses of metal spraying, a zinc-15%-aluminium alloy wire has been widely used. The original commercial experience was with 65-35% alloys used in powder form. Both have many of the advantages of the parent metals. At one time, the zinc-5%-aluminium alloy was also of interest. These alloy coatings may prove particularly satisfactory for sprayed coatings on articles where service conditions are not known in advance.

The corrosion rate of a bare sprayed coating is comparable to that of solid zinc or aluminium, although the greater surface area exposed may cause apparent corrosion rates to be a few per cent higher. For most uses, however, the sprayed coating is sealed or painted and achieves the much higher corrosion resistance associated with duplex coatings. The extra life depends on the sealer or on the thickness and type of paint used, and on the environment.

The slightly rough sprayed surface coating gives an excellent key for painting. Many simple paint treatments which give excellent long-term service on sprayed zinc or aluminium would be totally inadequate if applied directly to steel. However, care is needed to avoid paints where the binder penetrates into the pores leaving unbound pigment on the surface. This ability to penetrate into pores, however is the basis of the widely adopted sealing technique using one of many low-viscosity materials. Vinyl copolymer,

phenolic, epoxy or silicone products are most frequently used as then no further treatment is necessary.

A low acid polyvinyl butyral-based pretreatment primer ('etch' or 'wash' primer are alternative names) is usually advantageous as the first treatment of a metal-sprayed surface before painting. Up to an equal volume of spirit soluble phenolic resin is used as a diluent to the polyvinyl butyral of conventional pretreatment primers. This has an incidental, but particularly valuable effect, in reducing the free acid available to penetrate into the pores of the coating. The modified pretreatment primer is highly water resistant and this helps to avoid damage due to condensation.

With zinc, paints must be chosen to avoid inter-reaction which, months or years after the coating has been applied, may form zinc compounds at an interface of a type that destroys the bond between the paint and the zinc. Alkyds in particular should be avoided.

A wide variety of paint systems may, however, be used over the pretreatment primers. Applying a coat of inhibitive primer such as zinc chromate after the pretreatment primer is less advantageous than applying an additional coat of finishing paint; indeed, unless the inhibitive primer is carefully formulated, it may contribute problems of intercoat adhesion and blistering.

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F. PORTER

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12.5 Miscellaneous Methods of Applying Metallic Coatings

The more important metallic coating methods such as electroplating, spraying, hot-dipping and diffusion have already been considered. There are, however, several other methods which have certain advantageous features and therefore find exclusive application in specific fields. These include new techniques such as laser hardening and alloying¹.

The miscellaneous coating methods to be considered here are:

1. Immersion plating.
2. Chemical reduction.
3. Peen (or impact) plating.
4. Vacuum evaporation or metallising.
5. Chemical vapour deposition (CVD).
6. Cathode sputtering.
7. Brush plating.
8. Plasma spraying.
9. Ion implantation.

Their characteristics are summarised in Table 12.10.

Immersion Plating

Principles Immersion plating resulting from a displacement reaction involving the metal to be coated can continue only as long as the less noble substrate remains accessible to the plating solution, and therefore as plating proceeds, the quantity of M_1 deposited, and of M_2 dissolved, falls. Dissolution of M_2 can be avoided by coupling it with a less noble metal M_3 , so that only M_3 dissolves, i.e. by internal electrolysis.

Radio-tracers have been used to study silver deposition², and it has been shown that when certain inhibitors or complexing agents are present the displacement reaction may be markedly affected³.

If a displacement reaction is to take place uniformly, the surface of M_2 should be chemically clean initially; in addition, a wetting agent may be employed in the plating solution.

Features of the method The solutions and procedures are uncomplicated, and can often be adapted for barrel plating. Addition agents⁴ are usually necessary in order to restrict the high initial rate of plating, which might

otherwise cause poor adhesion and spongy deposits containing trapped electrolyte, although it has been reported that adherent deposits of copper on aluminium can be plated from a solution of CuCl_2 in alcohol⁵. Some difficulty in achieving a uniform coating may arise with articles composed of two or more different metals. Coating thickness is limited to about 0.001 2 mm (average), because plating cannot proceed after the last exposed M_2 atom has been replaced by an M_1 atom.

Table 12.10 Miscellaneous coating methods*

Method	Significant plating mechanism involved	Common examples
Immersion plating	Displacement of metal ions in solution by metal to be coated: $xM_1^{n+} + M_2 \rightleftharpoons M_1 \downarrow + yM_2^{m+}$, where $xn = ym$	M_1 : Cu from aqueous CuSO_4 M_2 : Fe
Chemical reduction	Chemical reduction, often based on simple redox reactions: $M_1^{n+} + R = M_1 \downarrow + \text{oxidised } R$ where R = a suitable reducing reagent	M_1 : Cu from aqueous CuSO_4 R HCHO
Peen plating	Adhesion brought about by the intimate contact of two chemically clean solid surfaces: $M_1 \text{ powder} + M_2(\text{or } M_1 \text{ solid})$ $\xrightarrow{\text{impacted}} M_1 \text{ solid coating}$	M_1 : Zn M_2 : Fe
Vacuum evaporation	Evaporation at reduced pressure in accordance with the Clausius equation, followed by condensation on a cold surface: $M_1 \text{ solid} \rightarrow M_1 \text{ vapour} \rightarrow M_1 \text{ solid on } M_2$	M_1 : Al M_2 : Fe
Chemical vapour deposition (CVD)	Chemical reaction causing gaseous M_1 compound to split up and release M_1 to deposit on M_2 : $XM_{1\text{gas}} \xrightarrow{\text{Heated } M_2} M_1 \text{ solid on } M_2$	M_1 : Cr M_2 : Fe
Cathode sputtering	M_1 is volatilised by d.c. arcing, followed by condensation on cool M_2 : $M_1 \text{ cathode} \rightarrow M_1 \text{ vapour}$ $\rightarrow M_1 \text{ solid on } M_2$	M_1 : Au M_2 : Se
Brushing plating	M_1 is electroplated on local areas by a brush or tampon	M_1 : Ni M_2 : Fe or Cu
Plasma spraying	Metals, or refractory materials or composites are applied by melting in an ionised inert gas	M_1 : tantalum, molybdenum, alumina, zirconia M_2 : a variety of metallic substrates
Ion implantation	Ions in gaseous form are implanted into the substrate by an electric field at low temperature	M_1 : Cr, Al, Si, Ni M_2 : Steel, W, Al and other metallic substrates

* M_1 : coating metal and M_2 : metal to be coated.

Properties of deposits These deposits invariably possess an appreciable number of discontinuities, which diminish their protective value. At such discontinuities there is an inherent susceptibility to corrosion because of the galvanic relationship that necessarily exists between M_1 and M_2 . Corrosion resistance may, however, sometimes be improved by sealing⁶ (cf. anodising) or by chromate passivation.

Owing to the thinness of the coatings, properties such as reflectivity and smoothness are chiefly governed by the substrate, although addition agents find useful application in improving these properties.

Applications The method is clearly restricted to those systems in which a displacement reaction can occur⁷, but it is possible to extend the range by pre-coating M_2 with a thin coating of another baser metal by an alternative coating method. Some alloys can be deposited⁸. The displacement coating is often followed by a further metal-finishing step. Applications include 'nickel dipping' of ferrous metals prior to vitreous enamelling to assist bonding; 'copper lacquering' of ferrous rod for wire drawing in order to assist lubricant carrying and improve the final appearance and corrosion resistance of the drawn wire; deposition of certain precious metals and alloys on copper and its alloys in engineering applications, and of copper alloys to facilitate their soldering⁸; plating of aluminium with zinc using sodium zincate solution to facilitate the subsequent electrodeposition of a Cu-Ni-Cr system; 'quicking' of copper alloys with mercury to promote adhesion and covering power in subsequent electrodeposition; deposition of gold on to steel pen nibs; deposition of copper on to plastics substrates containing a suitable base-metal powder for electrical conduction⁹.

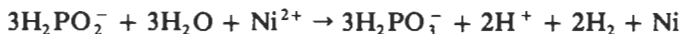
Chemical Reduction

Principles The reduction reaction is controlled essentially by the usual kinetic factors such as concentration of reactants, temperature, agitation, catalysts, etc. Where the reaction is vigorous, as, for example, when a powerful reducing agent like hydrazine is used, wasteful precipitation of M_1 may occur throughout the whole plating solution followed by deposition on all exposed metallic and non-metallic surfaces which can provide favourable nucleation sites. In order to restrict deposition and aid adhesion, the selected areas are pre-sensitised after cleaning; the sensitisers used are often based on noble metal salts.

Features of the method With proper plating control there is usually no limit to the coating thickness that can be built up, although the simple plating solutions seldom give acceptable thick deposits. Certain addition agents can be used; in the 'electroless' nickel process, for example, such additions include sequestering agents to prevent pre-precipitation of M_1 ; exaltants to enhance the reducing power of the reducing agent; stabilisers to inhibit certain active nuclei, thus preventing overall decomposition of the plating solution; buffers to control the pH of the plating solution; and wetting agents¹⁰. While high plating rates, e.g. 0.025 mm/min, can be achieved, moderate rates avoid poor adhesion and entrapment of solution in the deposit.

Although the actual plating operation may be uncomplicated, the plating solution requires regular replenishment of M_1 salts, and filtration.

The most extensively used reducing agent for the electroless deposition of nickel is hypophosphite¹¹, and the reaction is as follows:



The most important parameters of deposition are the temperature and the pH of the solution. Generally speaking, raising the temperature increases the rate of deposition. The solution can be alkaline or acid, the latter being preferred. The composition and operating conditions of a typical bath are:

$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	20–25 g/l
$\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$	25–30 g/l
Complexing and buffering agents	30–50 g/l
Accelerators	3–5 g/l
Stabiliser	3–5 g/l
Surfactant	30–50 mg/l
pH value	4.3–4.7
Temperature	93–95°C
Deposition rate	25–28 $\mu\text{m/h}$

Nickel can also be deposited by reduction with the aid of boranates¹² such as sodium boranate (NaBH_4) or *N*-diethyl borazane, i.e. $(\text{C}_2\text{H}_5)_2\text{NH} \cdot \text{BH}_3$, the basic reaction proceeding as follows:



The sodium boranate bath is operated at a pH of 14 and a temperature of 90–95°C. The rate of deposition is 10–30 $\mu\text{m/h}$. A metallic catalyst is required for the reaction.

Chemical reduction is used extensively nowadays for the deposition of nickel or copper as the first stage in the electroplating of plastics. The most widely used plastic as a basis for electroplating is acrylonitrile-butadiene-styrene co-polymer (ABS). Immersion of the plastic in a chromic acid-sulphuric acid mixture causes the butadiene particles to be attacked and oxidised, whilst making the material hydrophilic at the same time. The activation process which follows is necessary to enable the subsequent electroless nickel or copper to be deposited, since this will only take place in the presence of certain catalytic metals (especially silver and palladium), which are adsorbed on to the surface of the plastic. The adsorbed metallic film is produced by a prior immersion in a stannous chloride solution, which reduces the palladium or silver ions to the metallic state. The solutions mostly employed are acid palladium chloride or ammoniacal silver nitrate. The etched plastic can also be immersed first in acidified palladium chloride and then in an alkylamine borane, which likewise form metallic palladium catalytic nuclei. Colloidal copper catalysts are of some interest, as they are cheaper and are also claimed to promote better coverage of electroless copper.

Electroless nickel baths are usually preferred to electroless copper, since they tend to be more stable and are less likely to deposit metal on unwanted areas, such as plating racks. Electrolytic copper is then plated before the final application of nickel and chromium, where this is the required finish, as it

provides a ductile interlayer which serves to accommodate the large differences in the expansion coefficients of plastics and metals: this can lead to separation of the plate under severe temperature changes.

Other plastics now being plated on an increasing scale are polypropylene and, to a smaller extent, polysulphone. Polypropylene is considerably cheaper than ABS, and is much more resistant to distortion at elevated temperatures, so that it can be used at up to 150°C as compared with 100°C for ABS; the adhesion of the deposits is also superior.

Properties of deposits Deposits can be produced that are adherent, coherent and finely crystalline. Addition agents, e.g. organic sulphonamides¹³ can improve the deposit structure so that thick coatings can be produced free of nodules and blisters. The production of very smooth thick deposits of copper has been reported¹⁴. Thin deposits tend to reproduce the substrate topography, but some cases of levelling have been reported. The brightness tends to fall with increasing thickness.

Ductile and easily buffed chromium deposits having satisfactory corrosion resistance have been produced; thus 0.005 mm-thick chromium deposits applied to steel by chemical deposition or by electrodeposition gave similar results when subjected to a salt-spray test¹⁵.

Applications The method can be adapted to barrel plating and to the mirror-spray technique⁷. The development of printed circuitry has stimulated demand for means of rendering parts of insulating surfaces conducting and solderable. Developments seem to be confined to deposition of single metal species e.g. Sn, Ni, Co, Ag, Cu, Pd and Au. The hypophosphite method¹⁰ gives deposits which contain 8–10% of phosphorus. Such deposits are hard (e.g. 500 H_v) and brittle; they are relatively pore-free and have good corrosion resistance, particularly if heat-treated. In general, the corrosion resistance is proportional to the phosphorus content, and such coatings can comply with Fed. Spec. QQ-N-290. Exposure tests have shown that 0.012 mm thick Ni-P coatings give better protection to steel than 0.025 mm of electrodeposited nickel. Their high resistance to wear has been proved by their application in, for example, surfacing moulding dies. These coatings have been used to protect a low-alloy pearlitic steel from corrosion in air at 650°C, and in superheated steam for up to 1 000 h¹⁶ (see also Section 13.7).

Composite deposits of electroless nickel and PTFE are characterised by a very low coefficient of friction¹⁷. They contain 18–25% by volume of PTFE, and have found considerable application in the automobile, textile machinery and paper-making industries, among others.

Peen Plating

Principles The process consists of 'tumbling' the metal to be coated with a powder of the coating metal. It is considered that a form of welding is involved, but the type of conditions conducive to successful deposition indicates that the deposit adheres by mechanical keying (M_1 must therefore be relatively soft) and adhesive forces¹⁸. Thus pretreatments such as abrading or pickling enhance the keying effect, and the use of a soft metal

'strike' coating (e.g. Cu electrodeposited on steel) can also aid bonding. The presence of grease or oxide films on M_2 prevents adhesion of M_1 , and the use of 'promoters' and wetting agents ensures that such films do not interfere.

The optimum quantities and grades of M_1 powder, impact media, water and promoter, and plating conditions such as barrel-rotation speed, are best decided by trial runs.

Features of the method This method has the advantage that sintered, carburised, nitrided and non-metallic articles can be plated, and that no involved surface preparation is required. Furthermore, the possibility of hydrogen embrittlement is avoided¹⁹

Hydrogen-embrittlement can, however, arise during the acid pickling part of the processing cycle. It has been found that such embrittlement is more readily relieved by baking at a moderate temperature, or even by standing for a time at room temperature, than is the case with electrodeposited coatings. Although the reason for this is not established, it may be due to the fact that the peen-plated coatings are somewhat discontinuous, so that they allow molecular hydrogen to escape more easily than do electrodeposits. Plating speeds are of the order of 0.0075 mm/h, and thick deposits (0.05 mm) can be produced, although subsequent heat treatment may be required to enhance adhesion. Alloy coatings can be produced by using a coating powder prepared from its appropriate alloy.

Properties of deposits These are usually satisfactorily adherent, coherent and continuous on accessible surfaces. Micro-structures are often similar to those of metal-sprayed coatings. The coatings sometimes contain traces of included promoter solution which may partly account for the good tarnish and corrosion resistance. Exposure tests in a severe industrial atmosphere containing sulphurous gases showed that, for zinc on steel, similar corrosion resistance was provided by electrodeposition, hot-dipping and impact plating. In other tests, e.g. in marine atmospheres, impact plating provided superior corrosion resistance, and this method has met with approval for certain applications. Post-plating chromate passivation has been observed to confer more benefit on impact deposits than on electrodeposits of zinc on steel.

Owing to the slight abrasion during tumbling, very thin coatings are rarely mirror-bright, and the coating smoothness and reflectivity usually fall slightly as the coating thickness increases.

Applications Since M_1 must be relatively soft the method is restricted to metal powders such as Zn, Cd, Sn, Al, Pb and certain alloys. The geometry and strength of M_2 govern whether this method can be usefully applied. Generally impact deposits are applied for their corrosion resistance rather than for their decorative value. Thus the method has found particular application for coating ferrous nails, washers, chain links, and high-tensile steel springs and hose-clips, particularly where hydrogen embrittlement must be avoided (see Section 12.3).

Coatings consisting of a mixture of equal parts of cadmium and tin are particularly suitable for the protection of steel fasteners in contact with aluminium in aircraft structures where electrochemical corrosive attack is prone to occur under adverse conditions. The protection afforded is

considerably better than that obtained from zinc or cadmium coatings. A reduction in the couple voltage from 30 mV for pure cadmium in bimetallic assemblies to 20 mV for the tin-cadmium co-deposit has been found. The corrosion resistance both in neutral salt-spray and in outdoor exposure tests is markedly superior.

Cadmium and zinc combination coatings are considerably cheaper than tin-cadmium, and appear to be almost as effective, especially when in contact with aluminium under humid conditions.

Vacuum Evaporation

Principles Details of the process and plant, which consists essentially of a heated M_1 vapour source²⁰ contained within a closed coating chamber capable of evacuation to 13–1.3 kN/mm², for example, have been given elsewhere^{21,22}. The subject has also been reviewed by Fabian²³.

Special preparation of M_2 is necessary to obtain maximum adhesion and to avoid outgassing of foreign matter during evacuation. Outgassing can be prevented by pre-coating the substrate with a lacquer which can further provide a smooth base for M_1 .

Condensation of M_1 vapour can occur on all cool surfaces and the plating process is therefore not selective with regard to M_2 . Some fundamental aspects concerning the formation and properties of these coatings have recently been considered²⁴.

Features Good control of average coating thickness can be obtained and there is no excessive build-up at sharp discontinuities, but irregularly shaped articles should be so located in the coating chamber as to avoid 'shadowing' and to minimise loss of M_1 on the coating chamber's inner surfaces. The coating rates depend on the nature of M_1 ; for example, 0.025–0.075 mm thickness of Cd, Zn or Se can be deposited in 10 min, but considerably lower rates are observed for Cu, Al or Pt. The cost of depositing thick, protective coatings of, for example, Al is estimated to be similar to that for electroplating. The process has the advantage of being a dry one, and subsequent steps such as rinsing, de-watering and drying can be eliminated. Adhesion can be still further improved by, for example, prior shot blasting (where hydrogen embrittlement must be avoided) or by post-plating heat treatment. The plating can be carried out in stages to allow inspection, because lamination is not usually encountered.

Properties of deposits Deposits are normally smooth (often highly reflecting, depending on the topography of M_2), adherent, coherent, non-porous (although porosity may be affected by plating conditions), and free from inclusions. Significant alloy formation at the M_1/M_2 interface can be avoided. The electrical resistance is often greater than that of the same metal as cast or rolled.

Compared with other methods, vacuum evaporation produces coatings that have a most satisfactory corrosion resistance, e.g. 0.005 mm of evaporated Cd gives a degree of protection to steel similar to that afforded by 0.01 mm of electrodeposited Cd. Cadmium coatings on ferrous and other substrates can meet authoritative specifications concerning corrosion

resistance, adhesion and other factors, and the National Research Corporation has found that 0.012–0.025 mm of Al on steel withstood the standard 20% salt-spray test for 1 600 h.

Applications While any metal can be evaporated irrespective of its physical form, the method is restricted chiefly by the capacity of the vacuum plant and by the economic time available for the required thickness. Alloys such as Al-Cu, Sn-Cu and Ni-Cr, which do not fractionate unduly can also be deposited, while other alloys showing a greater tendency to fractionate may be dealt with by rapid evaporation, which minimises the fractionating effect.

The relatively low temperature rise of M_2 during plating allows the coating of temperature-sensitive materials. Furthermore, composite articles, even those having porous and otherwise reactive surfaces, can be successfully plated.

Aluminium is widely applied for decorative and protective requirements, while cadmium²⁵, zinc and titanium²⁶ have been applied to ferrous materials chiefly for their protective value. The method finds particular application in the plating of high-tensile steels used in aviation and rocketry, car fittings and lamp reflectors, and gramophone record master discs, as well as in the preparation of specimens for electron microscopy and in rendering insulated surfaces electrically conducting, e.g. 'metallising' of capacitors and resistors.

Chemical Vapour Deposition (CVD)

Principles Plant and procedure have been described in the literature²⁷ and in Section 12.3. In a given process one of the following reactions steps may predominate:

1. Reduction, e.g. $\text{CrCl}_3(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{Cr} \downarrow + \text{HCl}(\text{g})$
2. Thermal decomposition, e.g. $\text{CrI}_2(\text{g}) \rightarrow \text{Cr} \downarrow + \text{I}_2(\text{g})$
3. Displacement, e.g. $\text{CrCl}_2(\text{g}) + \text{Fe}_{\text{M}_2} \rightarrow \text{FeCl}_2(\text{g}) + \text{Cr} \downarrow$

Similar steps can sometimes be distinguished in cementation procedures such as calorising and sherardising.

Plating is carried out in a closed system whose atmosphere is adjusted to contain the metal-gas and a second gas which may be an inert diluent or a reactive gas (as in 1 above). M_2 is heated, for example by high frequency, and this then initiates deposition of M_1 by one of the above steps. Spent reaction products are exhausted and where possible reclaimed and recycled.

The usual kinetic factors govern reaction and therefore plating rates.

Features High plating rates (1.75 mm of tungsten/h) can be sustained²⁸, but efficiency can vary widely (between 5 and 90%) unless optimum control over reactant concentrations is exercised. The average coating thickness can be controlled accurately, but where the M_2 article is irregularly shaped, agitation and proper positioning are essential. Reaction step 3 does not require strict cleanness of M_2 for satisfactory adhesion. When M_1 is required for its corrosion-protective value then strict plating control is essential to ensure that M_1 is continuous and pure. Hydrogen embrittlement can be avoided.

The precursors, which include halides, carbonyls and organo-metallic compounds, among others, have the property of being reasonably stable in the gas phase until heated to temperatures at or near that of the substrate, which is usually in the range of 400 to 800°C. In chemical transport type reactions a heat gradient is used to move the product from the lower to the higher temperature zone in the case of an endothermic reaction, and vice versa for an exothermic reaction. In the flow type process, the reacting gas enters the vacuum chamber at a relatively low temperature, and contacts the substrate at a higher temperature. The rate of deposition and the properties of the coating can be varied by controlling the operating parameters.

In plasma-assisted CVD, an electrostatically or electromagnetically induced plasma discharge is carried out in a low pressure system. The result is that the process may be operated at a considerably lower temperature. This has been employed in the deposition of SiO_2 and Si_3N_4 in the production of heat-sensitive microelectronic circuits.

Properties of deposits Deposits are often more adherent, coherent and temperature-stable than those produced by alternative coating methods. Adhesion can be adversely affected by spurious reactions between the metal-gas and impurities in M_2 (e.g. as observed during the deposition of molybdenum on steel²⁹) and also where the thermal coefficients of expansion of M_1 and M_2 differ widely. The purity of reactants can affect that of M_1 . M_1 crystal size is reduced by raising the reactant concentrations, or by lowering the plating temperature.

Very few corrosion performance figures have been published, but one established process for depositing Cr on steel is stated to give a product possessing similar properties to those of 18/8 stainless steel.

Applications Important applications include chromium deposition for protecting ferrous substrates against oxidation, wear and abrasion, production of a thick ductile coating of Ni [e.g. from $\text{Ni}(\text{CO})_4$] for surfacing moulds, dies and tools³⁰, and deposition of metals which are very difficult to deposit by alternative methods, for example, tungsten, which can be used to confer protection on certain jet and rocket engine parts which are exposed to exhaust gases.

In general, many metals and alloys (e.g. of Al, Ta and Mo) can be deposited on metallic and some non-metallic substrates. M_1 may also be a metal compound having special useful properties (e.g. borides, nitrides, oxides, silicides and carbides), or even a non-metal such as Si (as in 'Ihrigising').

Cathode Sputtering

Principles Procedure and plant involved are similar to those used for vacuum evaporation. The pressure of the coating-chamber atmosphere, which may be air or an inert gas, is reduced and an arc is struck. The M_1 vapour formed subsequently deposits on surrounding cool surfaces, including those of M_2 .

Probably mechanisms which have been discussed may be either (a) electrochemical, with active gas particles forming unstable transient volatile M_1

compounds which finally decompose to deposit M_1 on M_2 , or (b) physical, volatilisation of M_1 (e.g. by thermal evaporation) being induced by arcing; but in this case high arc voltages are probably essential. The fundamental theory was developed by the experimental work of Wehner³¹ on measurement of sputtering yields and its dependence on ion energy.

Features The rate of deposition is low compared with that of vacuum evaporation, and is affected by variables such as pressure and temperature of coating-chamber atmosphere, arc voltage, cathode current density and geometry of cathode and M_2 . A high vacuum is not essential, particularly where an inert gas can be used. The M_1 disintegration rate is affected by the atomic weight of coating-chamber gas.

Properties of deposits These are usually adherent and coherent. M_1 is pure provided that all adverse chemically reactive gases are removed prior to sputtering; nitrogen, for example, can form a nitride with copper, and oxygen can form oxides with most metals.

Applications Although a wide range of metals can be sputtered, the method is often commercially restricted by the low rate of deposition. Applications include the coating of insulating surfaces, e.g. of crystal vibrators, to render them electrically conducting, and the manufacture of some selenium rectifiers. The micro-electronics industry now makes considerable use of sputtering in the production of thin-film resistors and capacitors³¹.

Sputtering has also been employed for the deposition of dry lubricants, and of hard and wear-resistant coatings. It is also employed for EMI/RF shielding of plastic components in the electronics industry³².

Brush Plating

Principles In brush or tampon plating, a pad or stylus soaked in the plating solution is attached to the anode (usually inert), the article to be plated being the cathode. A voltage of about 6 V is applied and the pad moved over the localised area to be plated. The pad can be of cotton wool or plastic foam, and any part which does not require to be plated can be masked off with a suitable lacquer. After plating for half a minute or so, the solution in the pad is replenished.

Features of the method Most metals can be deposited by this technique, usually on to steel or copper alloys as substrates. The most commonly deposited metals are nickel, chromium, tin, copper, zinc, cadmium, gold and silver.

The solutions used are generally highly concentrated, except in the case of the precious metals (for reasons of expense) and when zinc and cadmium are deposited from cyanide solutions, since soluble anodes are employed in the cases of these two metals. Proprietary solutions are available, particularly for such difficult metals as chromium, rhodium and indium, and it is advisable to use them.

The metal to be plated is first cleaned carefully and then activated with a weak acid. Steel can be treated with 3–5% HCl, whilst a 10% fluoboric acid solution is suitable for copper alloys. It is then ready for the electro-deposition process.

Properties of the deposits The deposits are generally similar to those obtained from conventional electrolytes, and are for the most part matt or semi-bright.

Applications Brush plating is mainly used on expensive assemblies where dismantling is either too expensive or impracticable. It can also be employed for building-up worn parts, and for the repair of local defects in printed circuits.

Plasma Spraying

Principles Plasma is a gas which has been raised to such a high temperature that it becomes electrically conductive as a result of ionisation. In plasma spraying a gas is passed through an electric arc, the resulting plasma being formed into a jet as it emerges from a nozzle. The materials to be deposited are introduced into the jet in the form of a powder, which melts and strikes the surface to be coated at high speed. The result is a tough and adherent deposit³³.

Features of the method An inert gas such as argon is generally employed to produce the plasma to avoid contamination or oxidation of the substance to be applied. The coating material reaches the surface at a comparatively low temperature, which can be below 100°C, although the plasma itself is at a temperature of many thousands of degrees; hence sensitive or low-melting basis materials can be plasma coated. The coatings are also usually denser and more adherent than those obtained with chemical flame spraying. Two or more powders can be applied simultaneously, so that metal composites can be produced in this way which are either in the form of coatings or free standing.

Properties of the deposits Almost any material which can be melted is suitable for plasma spraying, giving a vast range of possible coatings of single or mixed metallic or non-metallic substances. It is often possible to produce types of coatings which are not obtainable in any other way. Typical of the materials which are plasma sprayed are copper, nickel, tantalum, molybdenum, Stellites, alumina, zirconia, tungsten and boron carbides, and stainless steels.

Applications Plasma spraying is used to apply coatings for protection against wear and corrosion, to prevent erosion or cavitations, and to provide electrical insulation or conductivity. It can also be employed to produce bearing surfaces, abrasive properties or resistance to wetting by molten metals. The coatings can also be applied to facilitate the joining of different materials.

Ion Implantation

Principles In this process, ions of almost any material can be implanted into a substrate to alter its surface properties, such as resistance to wear, corrosion, and oxidation, as well as many others. The implanted material is not

a coating, but introduced below the surface, so that no dimensional changes occur³⁴.

Features of the method The dopant is first ionised, whereby the electrically charged species can be accelerated by electric fields, typically in the energy range 50–100 keV, and uniformly implanted over the required surface area to a depth of about 1 μm . The process is carried out at low temperatures, thus avoiding distortion and dimensional changes. The dopant is introduced into the electrical discharge in gaseous form and accelerated at high voltage on to the surface of the component to be treated.

Properties of the deposit The changes in surface properties of implanted materials which can be achieved are very considerable. Physical and chemical properties can be widely varied to produce special characteristics, some of which cannot be obtained in any other way.

Applications Ion implantation is widely employed to improve the life of tools. Thus press tools, dies and gear cutters can be treated to increase their durability by three times or more. Nitrogen-implanted tungsten carbide drawing dies for copper and iron wire can be improved up to fivefold. By implanting chromium, aluminium or silicon a considerable increase in the corrosion resistance of steel can be obtained. Implantation of chromium into aircraft bearing alloys has improved their durability in marine environments³⁵.

Ion Vapour Deposition A variant of the process is ion vapour deposition, in which a high negative potential is applied to the workpiece during chemical vapour deposition. The process has been employed on a commercial scale chiefly for depositing aluminium on to steel and titanium in the aerospace industry as an alternative to cadmium plating, which is liable to cause hydrogen embrittlement, especially of high tensile steel components. The aluminium is evaporated from a wire-fed resistance-heated boat³⁶.

The aluminium coatings are highly corrosion resistant, and are less liable to contact corrosion than cadmium when in contact with light alloys. They can also be used at temperatures of up to 496°C as against 232°C for cadmium. The aluminium coating is also unaffected by aviation fuels, unlike cadmium.

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13 PROTECTION BY METALLIC COATINGS

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13.1 The Protective Action of Metallic Coatings

The application of metallic coatings for the protection of metals may be required for one or more of the following reasons:

- (a) To prevent or reduce corrosion of the substrate metal.
- (b) To modify the physical or mechanical properties of the substrate metal.
- (c) To achieve and maintain some desired decorative effect.

Although the initial choice of coating material applied for reasons (b) or (c) may be dictated by the particular properties required, the corrosion behaviour of the composite metal coating/metal substrate system must also be taken into consideration in so far as it may affect the maintenance of the desired properties. Consequently, in all cases where protective metal coatings are used the corrosion performance of *both* coating and substrate require careful consideration.

Choice of substrate metal is usually governed by cost, weight and general physical, mechanical or fabrication properties, and these factors will normally dictate a very limited number of possible materials none of which may be ideal in resisting the corrosive environment which will be encountered in service. Ideally, a protective metal coating should exclude completely the corrosive environment from the substrate metal and, if this can be achieved, only the resistance of the coating metal itself to that corrosive environment needs to be considered. However, in practice, discontinuities in the coating may occur during application (Chapter 12) or be produced subsequently by mechanical damage or by the corrosion of the coating itself. In these cases the corrosion performance of the bimetallic system so produced becomes of major importance.

Anodic and Cathodic Coatings

A detailed discussion of galvanic corrosion between dissimilar metals in contact in a corrosive environment has been given in Section 1.7, but in the case of coating discontinuities the effect of the anode/cathode area relationship and the nature of any corrosion products formed at small discontinuities may modify any choice made on strict considerations of general galvanic corrosion theory based on the potentials of the coating and substrate in the environment under consideration.

Thus, coatings which are anodic or cathodic to the substrate are both used in practice, but whereas the former will provide sacrificial protection at a coating discontinuity the latter may stimulate attack on any exposed substrate. The sacrificial consumption of an anodic coating at a pore or discontinuity results in a gradual increase in the area of substrate exposed and a corresponding decrease in the corrosion current density which, in time, may become insufficient to maintain protection in the centre of the exposed area. The rate of sacrificial consumption of an anodic coating is reduced by several factors such as the resistance of the electrolyte solution within the discontinuity, blocking of the discontinuity by corrosion products or the formation of protective films on the exposed substrate which may be encouraged by increase of electrolyte pH by the cathodic reaction at the discontinuity. Under these circumstances the life of the anodic coating will be prolonged.

Zinc and cadmium are both anodic to steel and provide sacrificial protection to the substrate when used as coating metals. On exposure to industrial atmospheres, zinc will protect steel for a longer period than cadmium, whereas in many marine or rural environments cadmium provides a longer period of protection. Layton¹ attributes this difference in behaviour to the nature of the corrosion products formed in the different environments. In industrial atmospheres soluble sulphates of both zinc and cadmium are produced and are removed by rain so that corrosion can continue freely. Under these conditions zinc, which has a more negative potential than cadmium in most environments, is a more efficient anode than cadmium and gives a longer period of protection to the substrate. In rural and marine exposure, however, the cadmium carbonates and basic chlorides which are formed are insoluble and corrosion is stifled to a greater extent than is the case with the more soluble zinc carbonates and basic chlorides, so tending toward a longer life with cadmium coatings.

When cathodic coatings are used the sacrificial action is reversed, the substrate being attacked and the coating protected. This attack on the substrate can be highly localised and can lead to rapid penetration through the thickness of the metal. The effect is appreciably reduced by electrolyte resistance and by the stifling action of corrosion products, as mentioned above for anodic coatings, and the production of substrate corrosion products within the discontinuity can significantly decrease the corrosion rate and delay penetration.

Decorative coatings of nickel plus chromium are cathodic to steel or zinc alloy substrates and with these protective systems deliberate use may be made of discontinuities in the chromium topcoat where corrosion of the underlying nickel will occur. If the number of these discontinuities in the chromium layer is greatly increased the current density at each individual corrosion site is reduced, penetration of corrosion through the thickness of the nickel layer is thus slowed down and the period of protection of the substrate metal is prolonged.

In general, the choice between cathodic or anodic coatings will be governed by the service application. Where cathodic coatings are used any attack on the substrate will be highly localised, leading to rapid perforation of thin sections with a consequent loss of functional integrity. Anodic coatings, on the other hand, will protect exposed areas of substrate metal

by sacrificial action until the area exposed exceeds that over which cathodic polarisation of the corrosion reaction can be maintained, after which time the substrate itself will corrode freely.

With both anodic and cathodic coating systems, account must be taken of the extent to which the presence and nature of corrosion products on the surface may impair either the decorative aspects or the functional use of the article. For example, the presence of small amounts of corrosion products on the surface of gold-plated electrical contacts can markedly increase the electrical contact resistance and cause malfunctioning; the problem may be overcome by increasing the thickness of the gold deposit — thus reducing its porosity — or by interposing an undercoat of a more resistant metal to act as a barrier layer between the gold and the substrate.

Because of the many variables which can influence the corrosion reaction, the use of the e.m.f. series of metals to predict the behaviour of galvanic couples in a given service environment can be hazardous and misleading. Numerous examples of coatings expected to act cathodically which have, in fact, been anodic have been reported in the literature²⁻⁵ and specialised lists of galvanic couples in different environments have been compiled⁶⁻⁸.

Factors Affecting Choice of Coating

Many factors are involved in the choice of coating material to be used for any particular application, and these will now be described.

Resistance to the Corrosive Environment

The principal difficulty in assessing the resistance of a coating material to a corrosive environment lies in an adequate accurate definition of that environment. Metals exposed to natural atmospheres will corrode at markedly different rates dependent upon the degree of pollution present and a number of interrelated meteorological factors. Atmospheric corrosion rates for most of the metals in common use have been published by many authors and by official organisations such as the A.S.T.M.⁹ These tables may be consulted for general guidance but must always be used with caution, choosing data for environments which most nearly approach the service conditions concerned. However, purely local conditions can markedly affect the rate of attack. An example of this in the author's knowledge involved the corrosion of galvanised-steel air-intake louvres on the roof of a building in a severe industrial environment; most of the louvres gave satisfactory service but premature rusting occurred on those which faced in a westerly direction where the prevailing winds exposed them to additional chloride contamination picked up from a nearby river estuary. A detailed knowledge of both the macro- and micro-environmental conditions to be encountered is thus seen to be essential if the best choice of coating is to be made and it is often desirable to make site inspections before recommending a coating system for a particular application.

When the corrosive environment consists of waters or other liquids, the effect of the presence of minor constituents in the liquid as well as the degree of aeration and rate of flow must be taken into account.

Practicability of Application

It is essential to choose a material and a method of application which will provide a coating of adequate thickness with good coverage and distribution over the surface of the article.

Hot-dipped tin coatings are difficult to apply outside the thickness range of 8–38 μm ¹⁰ and hot-dipped zinc coatings do not normally greatly exceed 50 μm in thickness. Hollow sections and excessively large articles may be impractical to handle by the hot-dipping process and very thin sections may be subject to much distortion.

Electrodeposited coatings may range in thickness from about 0.1 μm to about 25 μm for decorative and protective purposes, though considerably greater thicknesses may be applied in the case of coatings for wear resistance purposes. The shape of the article to be plated greatly influences the thickness and coverage of the electrodeposit. Copper and nickel deposits cover well, throw well into recesses and levelling can be obtained during electrodeposition. Zinc gives good coverage but poor levelling and chromium has a very poor throwing power leading to bare areas in deep recesses of the plated article. Precious metals, because of cost, tend to be electrodeposited in thicknesses of less than 1 μm and at these thicknesses porosity of the electrodeposit is a significant factor; acid gold electrodeposits tend to be less porous than deposits from alkaline baths.

Sprayed metal coatings may be applied without limitations of size of article to be processed such as may apply for hot-dipping processes and the thickness and coverage of the coating can be readily controlled during application. Problems can arise, however, with applications involving complex shapes or hollow sections. Coating thicknesses are normally in the range 50–250 μm but considerably greater thicknesses may be built up for applications involving wear resistance, and diffusion heat-treatments may be subsequently applied in order to improve wear resistance further. Sprayed metal coatings are of a porous nature and contain a high proportion of oxides produced by the method of application. In service, corrosion products may build up in the pores of the coating which can contribute materially to a stifling of the corrosion reaction, but even so, sacrificial protection of the substrate exposed at any coating discontinuities may still be maintained.

Cladding by pressing, rolling or extrusion can produce a coating in which the thickness and distribution can be readily controlled over wide ranges and the coatings so produced will be completely free from porosity. Although there is very little practical limit to the thickness of coatings which can be produced in this way, the application of the process is limited to comparatively simple shaped articles which do not require much subsequent mechanical deformation. Among the principal uses are lead and aluminium sheathing for cables, lead-sheathed sheets for architectural applications and composite extruded tubes for heat-exchangers.

Compatibility of Galvanic Coupling

Most of the published data on galvanic corrosion concern solid metal couples rather than bimetallic coating systems, and it is important to bear

in mind that the same galvanic relationships do not necessarily apply in both cases; nevertheless, useful guidance can be obtained from the data for the solid-couple systems exposed to suitable environments. Data have been reported¹¹ for combinations of metals commonly used in the electrical industry; couples involving plated brass, copper and aluminium were exposed to a 1% salt spray and the corrosion currents (mA) were measured over a one-week test period. Relative ratings in this test are shown in Table 13.1 and items of particular interest in this table are that coatings of aluminium on either brass or copper are unsatisfactory because of the active galvanic corrosion which occurs at discontinuities. If tin plating is used as an undercoat to the aluminium, corrosion of the substrate is prevented, but if tin is applied as a topcoat over the aluminium (particularly by means of the conventional zincate process) it is sufficiently porous to allow the aluminium to continue to function as an active anode and corrosion can continue.

Table 13.1 Performance of various crimped metallic couples in 1% salt spray

<i>A. Completely Satisfactory Combinations</i>	
	Copper/nickel-plated copper
	Copper/gold-plated copper
	Tin-plated copper/aluminium
	Tin-plated copper/nickel-plated copper
	Tin-plated copper/solder-dipped copper
	Tin-plated brass/aluminium
	Solder-dipped copper/nickel-plated copper
	Nickel-plated copper/gold-plated copper
	Nickel-plated copper/silver-plated copper
	Gold-plated copper/silver-plated copper
	Aluminium/tin-plated aluminium (no copper undercoat)
<i>B. Satisfactory Combinations, Slight Galvanic Corrosion</i>	
	Copper/silver-plated copper
	Solder-dipped copper/tin-plated aluminium
	Copper/tin-plated copper
	Copper/solder-dipped copper
	Copper/reflowed tinned copper
	Silver-plated copper/tin-plated copper
	Silver-plated copper/solder-dipped copper
	Gold-plated copper/tin-plated copper
	Aluminium/tin-plated aluminium (zincate process)
<i>C. Borderline, Moderate Galvanic Corrosion</i>	
	Gold-plated copper/solder-dipped copper
	Tin-plated aluminium/nickel-plated copper
	Aluminium/solder-dipped aluminium
<i>D. Unsatisfactory, Severe Galvanic Corrosion</i>	
	Aluminium/brass
	Aluminium/copper
	Tin-plated aluminium/copper
	Aluminium/nickel-plated copper
	Aluminium/nickel-plated brass
	Aluminium/silver-plated copper
	Tin-plated aluminium/silver-plated copper
	Aluminium/gold-plated copper
	Tin-plated aluminium/gold-plated copper

The relationships given in Table 13.1 apply to the specific environment quoted and it must always be remembered that if the conditions are varied, even to only a small extent, different galvanic effects may be produced.

Effect of Coating Process on Substrate Properties

The application of any coating process may affect the physical or mechanical properties of the substrate material and any such effects should be considered when choosing the type of coating to be used and its method of application.

With hot-dipping processes, apart from the risk of distortion previously mentioned, the high temperatures involved can produce annealing, e.g. softening of brass and copper during hot-tinning. Furthermore, hard and brittle intermetallic-alloy zones are produced during hot-dipping as a result of diffusion of the liquid coating metal into the solid basis metal, e.g. FeSn_2 in the tinning of steel, Cu_6Sn_5 , and Cu_2Sn in the tinning of copper—the extent and depth of the alloy formation depending on temperature and time of dipping. Thus, too long a dipping time in hot-dip galvanising can lead to flaking during subsequent mechanical deformation^{12,13}.

Evolution of hydrogen during some electrodeposition processes can cause embrittlement if it diffuses into the substrate; the effect has been reported for chromium and cadmium plating of high-strength steels¹⁴ and provision is made in relevant standards^{15,16} for diffusion heat-treatments after plating to reduce the hazard (see Sections 8.4 and 13.3). Alternatively, zinc or cadmium coatings may be applied by vacuum deposition, thus avoiding any embrittlement of the steel—a process of this nature having been developed by the Royal Aircraft Establishment, Farnborough. Cases have also occurred where cracks in a highly stressed electrodeposit have acted as stress-raisers which initiate stress-corrosion of susceptible substrate metals.

Although the annealing effects of overheating are avoided when coatings are applied by metal spraying processes—provided that those processes are properly applied—it has been reported¹⁷ that compressive stresses imparted to the substrate by the grit-blasting pretreatment can alter the fatigue properties of the material. Cladding involves extensive cold-working which may necessitate annealing of the composite material before use.

Coating Properties

A number of physical and mechanical properties of coating metals need to be considered when making a choice of metal to be used in a particular application.

Appearance, colour and brightness are important in decorative applications. Copper, zinc, cadmium, nickel, silver and gold can be readily plated in a bright condition whilst tin normally plates as a dull deposit but may be brightened by flash melting after electroplating (flow brightening process). Aluminium and lead deposits are always dull, but reflective aluminium coatings can be produced by roll cladding using highly polished rolls. Colours may range from the blue-white of chromium through yellows for

gold or brass to the reds of bronzes. Reflectivity after polishing also varies with the coating metal, being very high for silver and rhodium and progressively decreasing in the order aluminium and palladium, tin, zinc, gold, iron and lead.

Hardness, strength and wear resistance are prime properties, not necessarily interrelated. For example, rubbing contact between two hard surfaces may produce more wear than with two soft surfaces though, in general, rubbing contact between one hard and one soft surface causes wear in the softer material. However, mechanical design factors can alter this wear relationship so that the harder material wears to a greater extent, e.g. the case of the rapid wear imposed on a steel record needle rubbing against a vinyl record surface. In general, the hardest deposits are those of chromium, nickel and rhodium; with iron, copper, zinc, cadmium and silver in an intermediate hardness group; with tin, lead, gold and indium being relatively soft.

Temperature resistance, i.e. a combination of melting point and oxidation resistance, may be of prime importance. A general correlation exists between melting point and hardness since both reflect the bond strength of the atoms in the crystal lattice, and the preferred order of coating metals for use in high temperature applications as temperature is increased is: silver, aluminium, nickel, rhenium, chromium, palladium, platinum and rhodium.

The electrical conductivity of coatings is often of secondary importance since they are of thin section and are in parallel with a metallic substrate of larger cross-section which is generally a good electrical conductor. A more important property for coatings used as electrical contacts is surface hardness and the ability to remain free from oxide and tarnish films. Thus, although aluminium has almost four times the conductivity of tin it is often tin-plated to improve its electrical contact properties. Other coating metals commonly used for low-voltage applications are gold; tin/lead, silver, palladium, copper, rhodium and nickel.

Economics

Economic factors are obviously of prime importance when choosing both the coating material and its method of application. Individual items in the economic balance sheet will vary not only with the material and the process but also with availability, local labour costs and factors unique to the design and use of the articles concerned. A further factor which frequently does not receive adequate importance in costing is the ease or otherwise of maintaining the finish so as to ensure an adequate and efficient service life for the component. In general, though with many exceptions, processing costs may be ranged in ascending order from hot-dipping to plating, spraying and cladding. The lowest cost group of metals includes zinc, copper, iron and lead, the intermediate group contains nickel, tin, tin/lead, cadmium and aluminium, and in the highest cost group are silver, palladium, gold and rhodium, though cost relationships may vary from time to time as a result of price fluctuations in response to supply and demand.

Experience in the application of metal-coating processes can materially affect economics. Thus, although it is possible to apply aluminium by

electrodeposition, the process is difficult to operate and few metal finishers apply the process; the application of aluminium coatings by hot-dipping or by metal spraying is much more readily accomplished and more of these types of installations are becoming available on the metal finishing market.

Coatings in Practical Use

In modern coating technology the range of materials used is ever increasing and specific coatings may be chosen and applied, often by specially designed techniques, for particular applications. Details of the behaviour of various specific metal coatings are given elsewhere in this book but some general information on a number of the more commonly applied coating metals is as follows.

Zinc (Section 13.4)

This is an anodic coating material that may be applied by hot-dipping, metal spraying or electrodeposition, with a good corrosion resistance to most neutral environments, particularly when used in combination with chromate or phosphate passivation treatments. In most cases of atmospheric exposure, zinc will provide good protection to steel, particularly where any sulphur pollution is present, but in rural and pure marine environments the conditions of humidity and chloride pollution level can reduce the effectiveness of zinc coatings and make the use of cadmium more suitable, though the same degree of protection may often be achieved at lower cost by increasing the thickness of the zinc coating. Zinc is the preferred coating for steel used under immersed conditions in scale-forming waters or sea-water and, since it is less toxic than cadmium it should be used in applications involving welding.

The life of zinc coatings is generally proportional to thickness and independent of the method of application, though it has been reported^{18,19} that zinc electrodeposited from the sulphate bath gives a better performance than when deposited from the cyanide bath. Hudson²⁰ has reported lives for 42 μm thick zinc coatings on steel ranging from $3\frac{1}{2}$ years in a severe industrial environment (Sheffield) to more than 10 years in a rural environment (Llanwrtyd Wells) and Gilbert²¹ quotes lives of 4–5 years in London, 9 years in Cambridge and 18 years in Brixham.

Cadmium (Section 13.3)

Cadmium also provides a sacrificial coating to steel which gives better protection than zinc in applications where strong acids and alkalis may be encountered and those involving immersion in stagnant or soft neutral waters. It should be used in applications involving bimetallic contact with aluminium and in electrical applications where ease of solderability is important. Cadmium has a low torque resistance and should be used as a coating material in cases where bolted assemblies have to be frequently

dismantled. It also provides better protection than zinc in enclosed spaces where condensation can occur, particularly when there is contamination by organic vapours.

Cadmium is more expensive than zinc. It is usually applied by electrodeposition in thicknesses up to about $25\text{ }\mu\text{m}$ and has a superior tarnish and stain resistance to that of zinc. As with zinc, the life of cadmium coatings is proportional to thickness; Hudson²⁰ quotes a life of only 9 months at Sheffield for a $25\text{ }\mu\text{m}$ thick coating and approximately 8 years for a $42\text{ }\mu\text{m}$ thick coating exposed to a marine environment at Calshot.

Tin (Section 13.5)

Tin is applied by hot-dipping or electrodeposition and has a similar corrosion behaviour to that of zinc. Coating thicknesses are usually in the range $12\text{--}50\text{ }\mu\text{m}$, and in the lower portion of this range coating porosity can be a factor to be taken into account (see discussions by Kochergin²², and Gonser and Strader²³).

Tin coatings are widely used in the electrical industry because of their good contact properties and in the food industry because of low toxicity. In addition to pure tin coatings a number of alloy coatings have been developed for special applications, e.g. tin-lead (terne plate), tin-zinc, tin-cadmium, tin-bronze and tin-nickel. Reference should be made to Section 13.5 and to the publication by Britton²⁴ for data on the corrosion of tin and its alloys.

Aluminium (Section 13.2)

Aluminium may be applied as coatings by metal spraying, cladding, hot-dipping and electrodeposition, though the last-named process is difficult to apply and by far the largest proportion of aluminium-coated metals are produced by the first two methods.

In atmospheric exposure to industrial environments its corrosion rate is only about one-third that of zinc and the corrosion reaction is stifled by the tenacious oxide which is produced; nevertheless it can frequently function as an anodic coating both for steel and for the less corrosion-resistant aluminium alloys.

Hudson²⁰ reported lives of about $4\frac{1}{2}$ years for $38\text{ }\mu\text{m}$ thick metal-sprayed aluminium coatings on steel exposed at Sheffield, and more than $11\frac{1}{2}$ years for coatings $75\text{ }\mu\text{m}$ thick. Sprayed aluminium coatings (approximately $125\text{ }\mu\text{m}$ thick) have also provided complete protection against exfoliation and stress corrosion to aluminium-copper-magnesium (HE15) and aluminium-zinc-magnesium (DTD 683) alloys in tests lasting up to 10 years in industrial and marine environments^{25,26}.

Nickel (Section 13.7)

Nickel has an inherently high corrosion resistance, particularly in chloride-free atmospheres and is widely used as a coating material in the chemical

industry. When exposed to the atmosphere, rapid tarnishing and slow superficial corrosion occur; for this reason, nickel coatings are seldom used alone, but they are widely used as undercoats beneath bright chromium to give decorative and protective schemes for steel, zinc-alloy and copper-alloy consumer goods notably in the automobile and domestic hardware industries. Used in this way, corrosion of the nickel undercoat is confined to localised pitting which develops at discontinuities in the chromium layer and which will eventually penetrate to the substrate. Many special processing variations have been developed to improve the corrosion resistance of these composite coatings and recommended systems are detailed in standards documents such as BS 1224 (1970)¹⁶.

Lead (Sections 13.4 and 13.5)

Lead coatings are mainly applied by cladding and find principal use in the chemical industry for resistance to sulphuric acid, for cable sheathing resistant to attack by soils and in architectural applications where resistance to industrial atmospheres is particularly good. They rely for their protective action on the formation of insoluble corrosion products which stifle the corrosion reaction and lead to very long service lives, but the corrosion resistance is impaired when chlorides are present.

Copper (Section 13.6)

Except in the case of certain decorative and electrical applications, copper is seldom used as a coating material in its own right owing to the rapidity with which it tarnishes, particularly in sulphur-polluted environments. Nevertheless its atmospheric corrosion resistance is good owing to the development of the well-known green patina of basic copper salts which gives protection against further corrosion of the metal. When copper coatings are used for their decorative effect the high lustre and distinctive colour are retained by applying a protective coating of transparent lacquer which may contain an inhibitor, e.g. benzotriazole.

By far the largest use of copper as a coating metal is in the form of undercoats to other protective schemes, such as the nickel plus chromium systems, where they offer great benefit by levelling the surface so as to improve the brightness of the finished article. Their rôle in the corrosion protection of the substrates is complex; they are themselves often preferentially attacked when overlay coatings are penetrated by corrosion and can stimulate enhanced corrosion of the substrate when penetration through their thickness occurs. On the other hand, however, in the case of coatings of bright nickel plus micro-discontinuous chromium, the use of a copper undercoat is known to improve corrosion resistance and to extend the period of protection of the substrate²⁷.

Chromium (Section 13.8)

Chromium is highly resistant to atmospheric corrosion, being almost inert in most atmospheres, and is therefore used as a thin, bright overlay to other

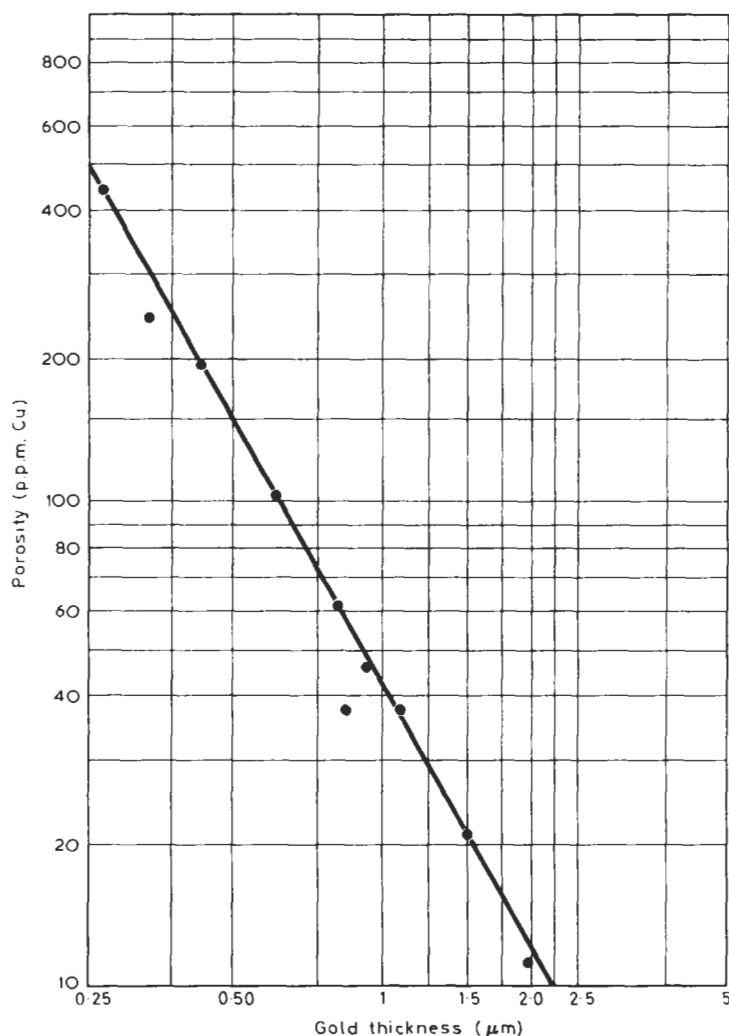


Fig. 13.1 Log/log plot of gold-plate porosity against thickness for the conventional hot-cyanide gold-plating bath on copper substrate. The porosity was determined by the amount of copper (p.p.m.) dissolved under standard conditions by an ammonia-ammonium persulphate test solution

coatings to retain decorative appeal for long periods. The thickness of these coatings, applied by electrodeposition, is normally in the range $0.3\text{--}1.3\text{ }\mu\text{m}$. In the lower thickness range the coating contains minute discontinuities which cannot be eliminated by increasing the thickness, since spontaneous cracking of the deposit occurs as the thickness builds up. The tendency to cracking of chromium electrodeposits is encouraged and put to good use by inducing cracking on a micro scale by processing modifications. When this is done the micro-cracked deposits so produced provide greater protection to nickel-plated steel and zinc-alloy substrates exposed to the

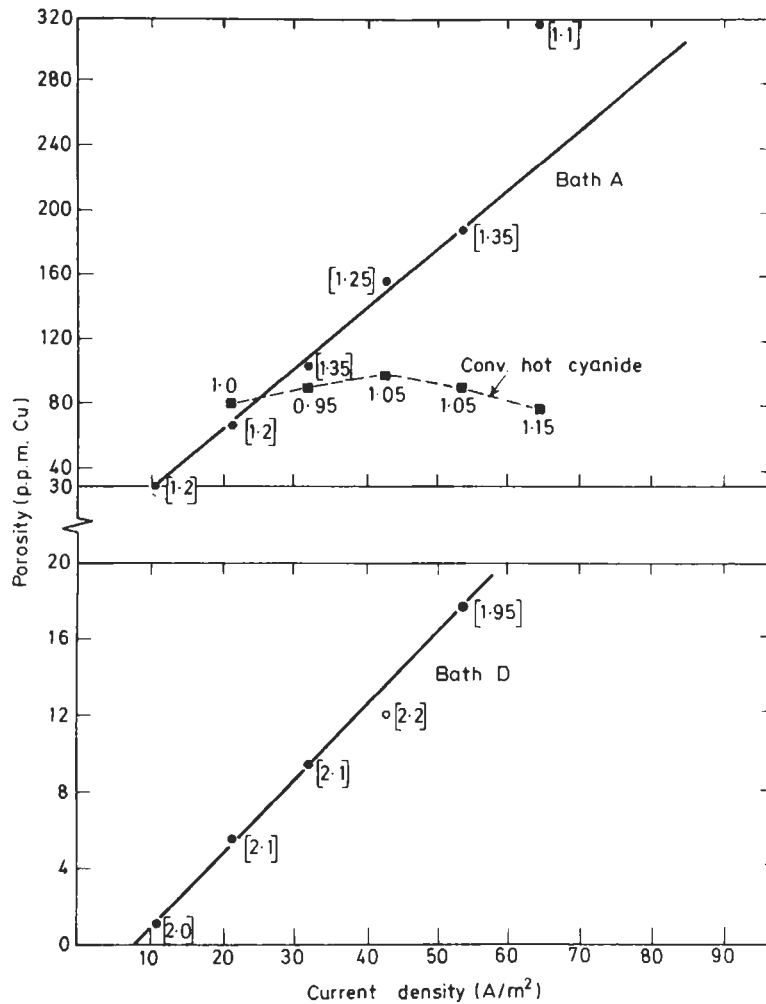


Fig. 13.2 Linear plots of the effect of current density on the porosity, expressed as p.p.m. Cu, for three different gold-plating baths. The numbers next to each point show the actual average thickness (μm) for each test. Bath A was a proprietary alkaline cyanide bath using silver as a brightener. Bath D was an acid gold bath containing cobalt and an ethylenediamine tetraacetic acid gold complex

atmosphere by increasing the area of nickel exposed at the micro-discontinuities and so reducing the corrosion current density at individual corrosion sites with a consequent reduction in the rate of penetration through the nickel layer.

Chromium is also a very hard metal with excellent wear resistance, and so is widely used as a coating material for engineering applications. For these purposes, coatings are applied by electrodeposition which may be several millimetres thick. These hard engineering chromium coatings invariably contain fine cracks and fissures which can allow corrodents to attack the

substrate, but this is not often a hazard in service and in many cases they are advantageous in providing a means of retaining lubricant on the working surface during use.

Precious Metals (Section 13.9)

Gold and platinum, being highly noble metals, can provide highly corrosion-resistant coatings, but are rarely used for this application alone because of cost. Silver, though cheaper than gold or platinum, has a somewhat lower corrosion resistance since it is very prone to attack by sulphides which cause dark tarnishing.

The principal use of gold is as a very thin coating about $0.05\text{ }\mu\text{m}$ thick for electrical and electronic applications. Because of the thinness of gold electrodeposits, porosity must be very carefully controlled since seepage of corrosion products from substrate or undercoat exposed at these pores can have serious adverse effects on both appearance and electrical properties of the composite. The porosity can vary with the thickness of the deposit (Fig. 13.1), and with the type of plating bath and with its method of operation (Fig. 13.2), and the phenomenon has been extensively studied by Clarke and many other workers.

Recent Developments

The general principles of protection of metal substrates by metallic coatings are of course, clear. Nevertheless detailed considerations and particular aspects have received continued attention and some of these developments can be highlighted. Amongst general treatments several books may be noted dealing with the coating spectrum and the theory of protection²⁸⁻³⁰, and a book on the testing of such coatings for product performance assessment in relation to quality assurance is also available³¹.

Galvanic Coupling

This particular topic remains vital but often controversial especially when attempts are made to codify practice and opinion. The British Standards Institution have published a 'Commentary on corrosion at bimetallic contacts and its alleviation'³² which represents an important first attempt to produce such a code. It lists 23 metals and alloys coupled to each other in three atmospheric and two immersed environments using a four-point subjective scale to describe behaviour.

The shortcomings of such a code are mainly attributable to the limited number of environments considered because specific behaviour is generally related to specific metal/electrolyte behaviour which can result in substantial potential changes or even polarity reversals. A polarity reversal implies a large potential at one or both metal electrodes and may be attributed to two main factors:

1. onset of passivity on the more base (negative) metal, thereby raising its surface potential to more noble values;
2. solution complexants reacting with free metal ions of the corroding metal thereby lowering that metal's corrosion potential.

The features of instances of such potential reversals have been described³³ and include tin coatings on steel in various foodstuffs, particularly acid fruits^{34,35}, cadmium coatings on steel in hard waters³⁶, and zinc and aluminium for cathodic protection of steel in natural ground-waters^{37,38}.

Porosity

The study of coating porosity and its effect on corrosion rates continues to be an important subject and is generally directed at establishing the minimum thickness that can be allowed in a specification, related of course to a test/service corrosion environment. Porosity usually decreases exponentially with coating thickness (Fig. 13.1 represents a relationship for part of the range only) and the minimum acceptable thickness can be defined according to 0, 0.5, 1.0% etc. porosity level or to a threshold corrosion rate. The ability to measure porosity rapidly and precisely is thus of importance and the whole subject has been critically reviewed by Clarke³⁹. In many cases the purpose of such testing is to separate effects on porosity of the coating process itself and the substrate preparation and roughness; the latter is often the aspect most susceptible to improvement.

Environment Classification

All testing has to be related to environmental conditions whose characteristics must be defined. The relation of accelerated corrosion test condition to real service conditions is one aspect while another is defining classes of environment and relating them to characteristic corrosion performance in order to produce useful specification guidelines. BS5493:1977 is an attempt to do this using four categories appropriate primarily to the UK (Table 13.2). Such a classification is clearly an over-simplification, but represents an important step in this particular direction.

Table 13.2 Atmospheric corrosion environments*

Type 1	Non-polluted inland	Rural areas, town suburbs
Type 2	Polluted inland	Industrial towns and cities
Type 3	Non-polluted coastal	Type 1 but with marine spray
Type 4	Polluted coastal	Type 2 but with marine spray

* BS 5493:1977

Alternative Coating Systems

The drive of financial economy has been manifest in terms of the need to establish alternative coating systems for particular applications based not on

technical performance alone but on cost saving and sometimes environmental or ecological considerations. Thus expensive metals may be challenged by cheaper metals and alloys, and cheap, metals by non-metals. Every coating is under such economic pressure, which some have withstood by reducing thickness, improving quality and maintaining performance, but some have succumbed to the competition. Gold in particular has faced competition from brass electrodeposits in the cheap market, titanium carbonitride (CVD produced) for wear-resistant applications and Pd-Ni alloy electrodeposit for electrical connectors and contacts, each representing cost saving and improvement in selected properties⁴⁰⁻⁴².

The desire to replace cadmium is generally attributed to its toxicity, both in terms of process pollution and product corrosion, and several alternatives are feasible: thicker zinc, tin-zinc alloy or tin-nickel alloy depending upon the precise application¹⁻⁴³. The demise of decorative nickel-chrome systems in the automotive industries of the world is partly due to cost and partly to market image, and not to technical performance where major improvements took place in the period 1960-1975 through the establishment of duplex nickel under-layers and micro discontinuous chromium top-layers. In the 1980s the trend has been towards black finishes produced generally by powder-applied epoxy polymers.

A recent publication by Dini⁴⁴ provides a relatively novel text covering the material science of coatings and substrates.

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13.2 Aluminium Coatings

Aluminium is used as a protective coating for iron and steel and also for some high- and medium-strength aluminium alloys; in some situations the optimum protection is obtained by using an aluminium alloy as the protective coating. Aluminium is applied also as a decorative coating on both metallic and non-metallic surfaces. Several methods of applying the aluminium coating are available, and the method selected depends to a large extent on whether the protective or decorative aspect is more important. Some methods of coating will be excluded by the geometry of the article to be coated, while others will be excluded by the chemical or physical nature of the article.

Coating Methods

Methods available for coating other metals with aluminium include spraying; spray aluminising (heat-treated sprayed coatings); hot dipping; Calorising (diffusion or cementation); vacuum deposition; electroplating; electrophoretic deposition; chemical deposition (gas or vapour plating); cladding or mechanical bonding; casting.

Painting with aluminium-pigmented paint is considered in Chapter 14 because its properties are essentially those of a paint and not of a metallic coating; in this respect aluminium paint differs from zinc-rich paint which can be formulated to provide galvanic properties similar to those of metallic zinc.

Sprayed, vacuum-deposited and plated coatings can be applied to most metals and to many non-metals, e.g. vacuum deposition is applied to many substrates including plastics; spray application can be used for coating fabric, plastic and paper. Hot dipping and other diffusion processes are dependent on the nature of the substrate for the properties of the coating. Most commercial applications of aluminium coatings are on iron and steel with smaller quantities applied to aluminium alloys and plastics.

Sprayed coatings These are of the greatest importance, particularly for the protection of structural steel or certain aluminium alloys. The metal to be coated must be grit blasted shortly before spraying to provide a clean rough surface. Chilled iron grit is used for most steelwork, while alumina or silicon

carbide may be used for metals having a hardness exceeding 360 H_V. Calcined alumina should be used for cleaning aluminium in order to avoid contamination of the surface by residual iron grit (see Sections 11.1 and 12.4). Grades of pure aluminium or aluminium alloys are applied by means of pistols fed by wire or powder; the two application methods give similar results. Coatings of 0.075–0.1 mm give good protection and it is preferable that not more than 0.05 mm should be applied in any one pass of the gun. In most atmospheric conditions no advantage is obtained by the use of aluminium coatings thicker than 0.25 mm and there is danger of flaking under some circumstances if the local film thickness exceeds 0.3 mm. For general purposes, the optimum performance is obtained using 99.5% purity aluminium applied within the limits of 0.1–0.2 mm.

Recent advances in metal spraying include arc spraying, which claims higher application speeds, better adhesion and reduced oxide content in the coating.

Spray-aluminised coatings For service temperatures in the range 550°C to about 900°C it is recommended that the coated steel item should be heated first to 800–900°C either in a mildly oxidising atmosphere or after coating with a solution of coal tar pitch in order to cause diffusion at the steel-aluminium interface. Oxidation of the aluminium coating during this heat treatment can also be reduced by the use of Al-0.75 Cd for the coating or by a protective coating of calcium hydroxide plus sodium silicate. The heat-treated sprayed coatings are sometimes known as *aluminised*, but the term *spray aluminised* is desirable in order to distinguish them from *hot-dip aluminised* coatings which are obtained (after pretreatment of the metal surface) by immersion in a bath of molten aluminium.

Hot-dipped coatings (Section 12.2) These coatings are applied after cleaning the work, e.g. pickling in hydrochloric acid in the case of steel, and then preheating. The work is then immersed in a molten salt bath, a flux or a reducing atmosphere, prior to immersion in the bath of molten aluminium. The bath temperature is usually in the range 620–710°C, depending on whether the coating material is an aluminium-silicon alloy (for use in high-temperature conditions) or pure aluminium (for corrosion prevention). Alloying occurs between iron and aluminium at the interface. The aluminium coating thickness is generally in the range 0.025–0.075 mm.

This type of coating is applied to both individual items and on continuous-coil plant. The process is in use in North America, Great Britain and other European countries.

Calorised coatings (diffusion, cementation – Section 12.3) These coatings are produced by packing the articles to be coated in a mixture of powdered aluminium, aluminium oxide and ammonium chloride for periods of 4–6 h at 800–950°C, followed by 12–48 h at 815–1 000°C after removal from the mixture. Coatings of 0.025–0.15 mm are reported with diffusion to a depth of 1 mm. The resistance of such coatings to scaling at temperatures up to 950°C depends on the maintenance at the surface of an aluminium content sufficient to give self-healing properties associated with the formation of a protective aluminium oxide layer.

Vacuum deposited coatings This type of coating can be deposited from

high purity aluminium vaporised by passing a heavy current through tungsten filaments around which the aluminium is wound. The application chamber is operated at very low pressure and the vaporised aluminium condenses on the cold surface of the work. Coatings of this type can be used to give an extremely thin bright finish to metallic or non-metallic surfaces. It is usual to apply a coat of stoving lacquer before and after depositing the aluminium coating. Coatings of the order of 0.025 mm are normally produced, but deposits up to 0.025–0.075 mm can be applied and are more appropriate where corrosion protection as well as decorative properties is required. Silicon monoxide is sometimes used as a final protective coating at thicknesses around 100 μm . Vacuum deposited coatings of aluminium can be applied to irregular static shapes or to plastic strip passing through the application chamber at speeds of 7.6 m/s or greater.

Sputter application is somewhat analogous to vacuum deposition. The deposition is carried out in a partial vacuum of about 13 N/m² and at a potential of around 1 000 V.

Electroplated coatings (Section 12.1) Aluminium can be electroplated from molten salts or organic solvents. It can be plated on to other metals from fused aluminium chloride melts, e.g. 75% AlCl_3 , 20% NaCl , 5% LiCl , operated at 170–180°C and 210 A/m².

Aluminium can be deposited from complex organic solutions if sufficient precautions are taken, and such coatings are now being produced commercially in North America. Two of the systems on record are (1) aluminium trichloride and lithium aluminium hydride dissolved in diethyl ether used at 40°C and 50 A/m², and (2) aluminium chloride, *n*-butylamine and diethyl ether used at 20°C and 970 A/m². Deposits of 0.010 mm can be obtained on mild steel or copper at 20°C and 970 A/m² using aluminium-wire anodes and nitrogen or argon atmospheres.

Electrophoretic coatings Coatings of this type can be produced by electrophoretic deposition of aluminium powder from a carrier system based on methyl alcohol and water. The material to be coated, e.g. steel, can be passed through the system using aluminium anodes and a potential of about 50 V. The deposited aluminium and strip then pass through compacting rolls, and are coiled prior to heat treatment at temperatures in the region of 400–600°C; the lower temperatures give maximum ductility to the coating while the higher temperatures improve adhesion at the expense of the formation of a brittle intermetallic layer between the coating and the steel substrate. Further improvement in adhesion can be obtained by heating the coated coil at 750–950°C for 30 min to 5 h with a corresponding increase in the intermetallic layer between the substrate and coating. A similar deposition of powder has been applied by electrostatic-spray techniques in air or in an inert atmosphere. Deposits have also been made as a slurry in an organic binder, e.g. polyethylene oxide, followed by drying and compacting.

Chemical deposition, gas or vapour plating This is a chemical process whereby the aluminium is deposited when an aluminium compound is pyrolysed. Organo-metallic compounds such as aluminium diethylhydride or tri-(iso) butyl aluminium (TIBA) are introduced into the work chamber after purging with an inert gas such as argon or nitrogen. The hydride

decomposes at around 180°C and TIBA at 260°C to deposit aluminium; deposits of from 0.075 to 2.5 mm are claimed on a variety of substrates. The coatings are said to be ductile, adherent and lustrous.

In a related process the work is dipped in a catalytic titanium compound and then transferred to a bath of aluminium hydride solution. The solution dries leaving the hydride on the surface and mild heating then turns the hydride into metallic aluminium. The conversion stage occurs slowly at room temperature or in seconds at 100°C.

The technique lends itself to the coating of surfaces which are relatively inaccessible, and it is stated that the process has been used to coat parts for turbine engines and could be used to coat parts for steel mills and coil coaters.

Cladding (mechanical bonding) The mechanical cladding of a surface with aluminium can be achieved by rolling, extrusion or drawing. Aluminium cladding can be bonded to other aluminium products and to a variety of substrates including copper and steel; the products can vary from sheet or strip to extruded shapes and wire. The cladding process is carried out by the metal supplier and this type of material is discussed in Section 4.1.

There is an increasing interest in explosive bonding as a means of bonding aluminium-steel and other composite cladding systems.

Casting Casting around steel parts, which are first hot dipped in aluminium or in aluminium-silicon alloy (the Al-Fin process), gives good bonding but requires careful design because of the different thermal-expansion coefficients of the two metals.

Nature of Coatings and Physical Properties

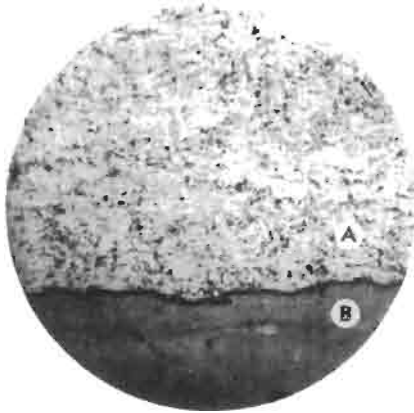
Sprayed aluminium coatings consist of small flattened globules of metal surrounded by aluminium oxide which forms about 1 to 3% of the coating. The coating density is typically 2.3–2.4 g/cm³. The outer surface is uniformly slightly rough with a whitish appearance. The coating is a reasonable conductor of heat and electricity, although inferior to bulk aluminium of similar purity. Coatings are cohesive and normally 0.10–0.20 mm thick. They have good adhesion on a properly prepared surface, but above 0.3 mm there may be danger of adhesion being weakened. Only slight deformation of the coating is possible. The mechanical properties of the base metal remain substantially unimpaired except for a slight loss in fatigue strength. Softening of strong, heat-treated aluminium alloys can occur with overheating through poor spraying technique. The structure of sprayed aluminium coatings is illustrated in Figs. 13.3 and 13.4.

Hot-dip aluminised coatings are obtained preferably by continuous methods. They are normally about 0.05 mm when unalloyed metal is used, but in the case of aluminium-silicon alloys only 0.025 mm is applied. As dipped, the surface may be rough; a bright appearance can be obtained by mechanical treatment such as rolling or drawing. Silicon appears to alter the viscosity of the bath and also inhibits the growth of the iron-aluminium alloy layer. The structure of the aluminium-silicon alloy coatings is distinctive. They show dark grey acicular needles of a silicon-rich constituent, and dispersed islands of an iron-aluminium constituent are also present in

Fig. 13.3 Sprayed aluminium; section taken parallel to substrate and etched; $\times 75$



Fig. 13.4 Transverse section of sprayed aluminium on steel; etched in HF. *A* aluminium and *B* steel; $\times 75$



the aluminium solid solution outer layer. The two layers close to the steel base are of different iron-aluminium-silicon alloys with an average iron content of 33.5%. In the absence of silicon the plates and stringers in the aluminium solid solution outer layer are iron-aluminium constituents containing about 45% iron. X-ray examination of both types of coating shows the presence of FeAl and lesser amounts of Fe₃Al, although this is not in accord with the equilibrium diagram. The coating is more dense than aluminium but no precise figures can be given. The coatings will withstand moderate forming (up to bends of twice the metal thickness, depending on the thickness of the brittle alloy layer); failure occurs more readily in compression than in tension. In the former case, shearing stresses develop at the alloy/base metal interface, but in tension, cracks which do not immediately affect adhesion develop at right angles to the surface in the iron-aluminium layer. The mechanical properties of the aluminised product are those of the base metal except for a slight loss of fatigue strength and a loss of tensile strength due to the annealing effect of the coating operation. At temperatures up to 500°C, coated steel will reflect about 80% of incident radiant heat. The coating is a good electrical conductor.

Calorised and heat-treated mechanically-clad products have coating structures similar to hot-dip aluminised coatings, but the degree of alloying with iron is variable (Fig. 13.5). With Calorised products the surface layers usually contain 25–50% aluminium.

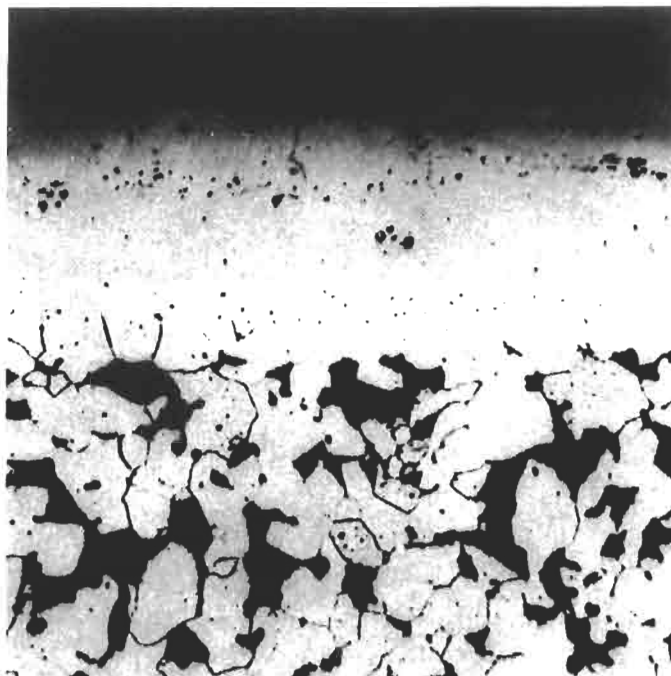


Fig. 13.5 Section through Calorised coating on mild steel; approximately $\times 500$ (courtesy Babcock and Wilcox Ltd.)

Vacuum-deposited and electroplated coatings are pure metal with no chemical bond to the underlying surface. The properties will be those of pure aluminium. The presence of lacquer, in the case of vacuum-deposited coatings will, however, afford resistance to the passage of electricity and limit the maximum temperature of use.

Steel with up to 0.075 mm thick aluminium coatings can be gas-cut by both hand and machine methods, and welded, without removal of the aluminium. No fume problems arise in welding aluminium-coated material; in practice, however, it is usual to leave the edges bare and to spray the joint with aluminium after welding.

Corrosion Resistance

The corrosion resistance of aluminium coatings is generally related to that of solid aluminium of similar thickness. Additional factors arise with sprayed coatings associated with texture, and with aluminised and other coatings when diffusion from the substrate can occur.

Ordinary temperatures The protection of steel by aluminium coatings

depends partly on sacrificial action and partly on a physical barrier associated with the aluminium and oxidation products. Initially, sprayed aluminium coatings in atmospheric or immersed conditions may show slight superficial rust staining through pores in the coating before penetration through the oxide skin around each aluminium particle enables aluminium to protect the steel cathodically. Subsequently, insoluble aluminium corrosion products block the pores and reduce corrosion currents to a negligible value, thus conserving the aluminium coating. This result is readily observed in practice when slight initial rust staining of the coating may occur and then either diminish or remain unaltered for many years. Rust staining can be avoided by the use of sealing lacquers. It is generally agreed that the cathodic polarisation of steel by aluminium is less than, for example, that effected by zinc although the standard electrode potentials indicate the reverse. This results in a long life for the aluminium coatings although they may allow some rust to form at breaks in the coating if the nature of the electrolyte in the environment is such that there is no galvanic protection of the steel, e.g. at cut edges of sheets in a mild atmosphere. The initial rusting is not progressive and in some cases the rust is reduced to magnetite leaving only a grey colour.

In selecting sprayed-metal coatings for steel, aluminium is preferred for use in aggressive environments such as marine environments, acidic environments and sulphur-containing industrial environments. Aluminium coatings are less suitable than zinc in most strongly alkaline environments. Coatings of aluminium-zinc mixtures or compounds of composition of approximately 65Zn-35Al have been used commercially, and it is claimed that the initial rust staining sometimes associated with aluminium coatings is avoided. Coatings of aluminium-zinc mixtures can also provide galvanic protection to some aluminium base alloys where aluminium alone does not provide the required sacrificial protection. Duplex sprayed-metal coatings of aluminium and zinc, or of two grades of aluminium, have been tested to see if they could prevent rusting or give improved protection; such duplex systems have not given worthwhile improvement over that of a single coating material.

Scott shows that unpainted sprayed coatings, 0.075 mm thick, of aluminium and zinc are giving good service in marine and rural atmospheres after 15 years, with the aluminium coating being slightly superior. In an industrial atmosphere BISRA tests show that the aluminium coating after 15 years is superior to zinc. When immersed in the sea, 0.075 mm zinc lasted less than four years, whereas the same thickness of aluminium was still affording protection to steel after 14 years.

Other investigations indicate that half-tide conditions give results similar to fully immersed conditions, and that in sea-water the 99.5% aluminium coating is preferred to aluminium-zinc or aluminium-magnesium alloy coatings.

Hudson, in tests at Sheffield (severe industrial atmosphere), observed that an 0.075 mm coating of aluminium had not failed after 18 years service (Fig. 13.6).

Sprayed coatings can be used as a base for painting and it is recommended that a minimum of 0.075 mm of aluminium be used. In practice a combination of 0.1-0.2 mm of aluminium plus paint coatings will give maximum economic durability on long-term structures.

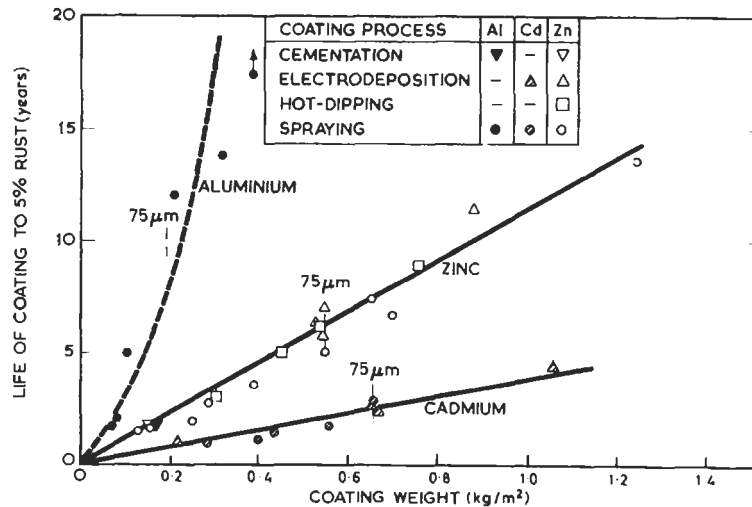


Fig. 13.6 Relation between coating life and weight for metal coatings on steel exposed at Sheffield. The line for aluminium has been amended and drawn as a curve (after Fig. 7 of Special Report No. 66 of the Iron and Steel Institute)

Tests by Clark for the Corrosion Sub-committee of the American Welding Society were carried out at severe marine and industrial sites. After four years, the greatest protection to steel was given by sprayed aluminium coatings combined with aluminium vinyl paint in the following environments: (a) sea air, (b) sea-water immersion, (c) alternate sea-water immersion and exposure to air (tidal conditions) and (d) industrial atmospheres contaminated with sulphur compounds.

Exposure tests of 5-years duration in the atmosphere and during immersion in fresh water or sea-water by Welding Institute and by Stanners and Watkins have indicated the best paint systems for aluminium-coated steel. For immersed conditions two systems giving good performance are:

1. Modified pretreatment primer plus zinc chromate primer plus two coats of micaceous iron oxide/polyurethane.
2. Modified pretreatment primer plus three coats of aluminium-pigmented vinyl copolymer.

Under atmospheric conditions the following systems gave good performances:

1. Pretreatment primer plus micaceous iron oxide/long oil tung phenolic.
2. Zinc chromate primer plus micaceous iron oxide/alkyd or phenolic.
3. Aluminium-pigmented vinyl.

Hot-dip aluminised coatings have been tested by the American Society for Testing and Materials over a 23-year period in rural and marine atmospheres. In most cases, coatings of 0.025–0.050 mm thickness show no deterioration, but at the more severe marine site some rusting has occurred.

Calorised coatings have a substantial iron content at the surface. Iron-aluminium alloys generally have superior corrosion resistance to that of the

steel substrate, and atmospheric exposure tests have shown Calorised coatings to afford useful protection.

Successful anodising of aluminium coatings produced by hot dipping and by electrophoretic deposition has been claimed, but this is subject to having an aluminium coating free from pores and a coating of sufficient thickness to enable the coating to be anodised; an anodic film 0.025 mm thick is formed at the expense of approximately 0.05 mm from a uniform aluminium surface. The steel must be fully stopped off in the anodising bath. Similar observations can be made with respect to aluminium coatings applied by other techniques.

High temperatures Diffusion coatings producing iron-aluminium alloys are used to provide protection to steel at high temperatures. These coatings can be produced by hot dipping, Calorising or by metal spraying followed by heat treatment.

Alloying of the coating and steel substrate commences at temperatures in the range 300–480°C, and the resistance of the substrate to oxidation increases with increasing aluminium content at the surface. An aluminium content of 8–10% is said to markedly reduce subsequent oxidation at temperatures as high as 1 000–1 100°C. The diffusion and alloying processes enable the aluminium coating to give good protection to steel at temperatures well beyond the melting point of aluminium and such coatings find service in atmospheres where sulphur-containing fuels are being used.

Up to 550°C, aluminium coatings may be used in the 'as applied' condition, and the hot-dipped aluminium-silicon alloy may be used up to at least 680°C, but for service at higher temperatures additional diffusion treatment is recommended for all except Calorised coatings.

Up to 750°C, the performance of all aluminium diffusion coatings is considered to be very good, but above this temperature the results appear to be dependent on the coating thickness, diffusion treatment and the specific service environment. Sprayed aluminium coatings can be used up to 900°C after diffusion treatment. Hot-dipped coatings also benefit from additional diffusion treatment, and omission of silicon from the coating alloy improves performance at the elevated temperatures.

Above 900°C, the life of aluminium-coated steel is more limited although the coating can still provide significant protection to steel, e.g. at 900–980°C the life is said to be increased 20 times, and at 980–1 000°C the life is said to be increased 5 times.

Applications

The main application of sprayed aluminium is for the protection of structural steel, and the process can also be utilised to protect high-strength aluminium alloys. The process has the important advantage that it can be carried out on site.

Sprayed aluminium coatings were applied over twenty years ago for a number of buildings in steelworks, notably at Margam, Trostre and Velindre in South Wales. At Margam all steelwork above crane girder level has been aluminium sprayed to 0.10 mm thickness and painted with two coats of

commercial-quality aluminium paint. Two sections in a severely aggressive environment were repainted about ten years after installation, although there was no rust present on the sprayed steelwork; the steelwork below crane level had, meanwhile, been repainted twice. It has been estimated that with an average interval of $8\frac{1}{2}$ years between repainting operations, the total painting cost over 50 years will be reduced by nearly 50%. The more recent Spencer Steelworks has been similarly protected following the experience gained in the earlier buildings.

Aluminium-sprayed steel windows in Sheffield remained in good condition some 17 years after erection. Aluminium-sprayed coating on a steel structure at a steelworks in Sheffield is intact after service for 34 years with paint maintenance at approximately 10-year intervals.

The Spanish National Steelworks has been given similar protection using sprayed aluminium coatings. Railway bridges at Carlisle and Hook showed no corrosion when examined after five years with an 0.075 mm aluminium coating on main surfaces and an 0.15 mm coating where exposed to direct locomotive blast. Aluminium-sprayed coatings have been used on two large road bridges on the southern end of the M1 motorway. Parts of the Severn Bridge have been sprayed with 65Zn-35Al alloy. Harbour bridges in Australia and the Near East sprayed with aluminium are in good condition 10–12 years after application. It is estimated that most structures protected by aluminium-sprayed coatings could have an extremely long service life if a simple paint coating was maintained at intervals of the order of 10 years.

The main roof girders of the BEA engineering base and workshop at London's Heathrow airport are aluminium sprayed.

Soft peaty water, e.g. as in Scottish hydroelectric schemes, has been satisfactorily carried in painted duplex-coated steel pipe (0.075 mm of zinc followed by 0.075 mm of aluminium), while a similar duplex coating was reported successful in a steam-ammonia atmosphere. A French railway bridge, however, showed peeling of the aluminium in a few months, owing to corrosion of the underlying zinc, suggesting that the duplex coatings should not be used indiscriminately; the powder-sprayed technique is recommended for duplex coatings.

Hydroelectric-plant pipelines of 0.4 km in length and 1.8 m in diameter were in good condition after service for eight years. At another hydroelectric plant, steel and cast-iron pipes carrying high-pressure soft water from a mountain reservoir had been in service for about 50 years with considerable internal corrosion. For safety reasons, it was decided that the pipes should be replaced or the corrosion stopped. In 1959 the pipeline was gritblasted internally and sprayed with 0.25 mm of 99.5% Al followed by two coats of petroleum bitumen. Thirteen years later the aluminium coating was still giving satisfactory service on these surfaces which were prepared and coated under the most arduous conditions.

Aluminium-sprayed coatings are used successfully on gas cylinders and on ammunition boxes under a wide variety of atmospheric conditions.

Car-ferry vessels in Australia have 0.15 mm of aluminium-sprayed coatings on the inside and outside of the hull followed by a compatible anti-fouling paint. Steel vertical legs on the *S. S. President Cleveland* and *S. S. President Wilson* are aluminium sprayed followed by two coats of aluminium-pigmented vinyl paint. Aluminium-sprayed steel is also giving

good service in tropical marine atmospheres on sheds erected in 1960 at Tema Harbour, Ghana.

Aluminium is particularly resistant to sulphur-polluted atmospheres, and sprayed coatings are used in sulphuric-acid plants for the main convectors; for hot, intermediate and cold heat exchangers; and for the internal surfaces of interconnecting ducting. Coatings of 0.15 mm thickness have given good service.

There are many instances of the use of aluminium spraying for the protection of steel in gasworks. These include the Dudley Gasworks' Retort House, which is in good condition after nine years or more; the largest welded gas holder in Europe located at Bristol was in excellent condition 10 years after treatment despite the severely corrosive environment, and a steel structure at the Coxside Gasworks at Plymouth needed no maintenance after more than 13 years service on a site only a few hundred metres from the sea. Other aluminium-sprayed applications include the gas holders, gas mains and blast furnace components at the Spanish National Steelworks at Aviles, and the components for the converter and heat exchangers of sulphuric-acid plants in Australia.

Chimney stacks have been sprayed externally with aluminium at many gasworks, oil refineries, laundries and petrochemical plants, to resist the combined effects of heat, condensation and atmospheric attack.

Steel structures and components subject to high temperature and corrosive attack on which paint would fail rapidly are given excellent protection by sprayed aluminium applied in accordance with BS 2569: Part 2:1965. Such coatings are used in blast-furnace downcomers, conveyor cooling hoods, and offtake ducting in reheating furnaces.

Converter shells for production of sulphur trioxide from sulphur dioxide have been in operation for over 12 years after spraying with 0.20 mm of aluminium. Operating conditions are sulphur trioxide at 600–650°C internally and 7% dry sulphur dioxide at 200–450°C externally, conditions which formerly resulted in lives of only two years without the metal spraying. A similar coating thickness has been used on coal-wagon tipper gear to provide protection against wet sulphurous conditions in the steel industry, and a coating life of 20 years is expected.

Aluminium coatings are not favoured in atmospheres containing explosive mixtures because contact with rusty steel can cause incendiary sparking, and for this reason aluminium coatings are not used for protection of structures in coalmines (cf. CP 2008:1966).

Aluminium spraying of steel street-lighting columns has been used since the 1950s and it is estimated that one producer alone has supplied up to 200 000 such columns; repainting is simpler, even on neglected columns, than on columns not metal sprayed. Aluminium spraying has been used on reflector towers used in the television link between Manchester and Edinburgh, and on similar structures.

Spray-aluminised coatings are used for exhaust valves in automobile engines, exhaust and silencer systems (double and triple life), tyre moulds, gas ducting, heat-treatment pots, furnace ladles, carburising boxes and fans handling hot gases. Similar applications utilise Calorised and hot-dip aluminised coatings. Hot-dip aluminised steel wire has been used in steel-cored aluminium conductors for overhead transmission lines. For some

applications the greater heat-transfer efficiency of the aluminium coating compared with that of solid steel is an asset.

Electrophoretic and similar compacted coatings are in early stages of development but will no doubt take their place alongside other coating methods.

Vacuum deposition of high-purity aluminium has been used as a bright finish of a decorative nature on domestic items and some car accessories, as well as special items for space missions where opacity to solar radiation was required. Continuous deposition on plastic strip at speeds up to 450 m/min has been achieved.

Plating of aluminium has been developed for electroforming wave-guides with wall thicknesses up to 0.10 mm, and for the aluminium coating of reflectors.

Aluminium cast onto steel or cast iron is used to produce integral aluminium/steel drums and bimetallic pistons. Aluminium clad onto other metals by mechanical bonding is used in heat-exchanger systems subject to multiple atmospheres or environments. The clad products are also used for cooking utensils and functional presswork.

The non-toxicity of aluminium coatings and freedom from taste or taint means freedom from health hazards during application and provides hygienic finishes for contact with foodstuffs, e.g. baking tins, oven trays, containers.

Aluminium coatings also provide a suitable key or pretreatment for subsequent coatings, e.g. aluminised steel provides a good base for vitreous enamel.

Recent Developments

Aluminium continues to find use in protecting structural steelwork, and medium-strength aluminium alloys. Elevated temperature applications with aggressive corrosive conditions shows that aluminium demonstrates a superior service performance to zinc. Al-Zn alloys have been developed which have superior corrosion resistance to both aluminium and zinc in certain operating conditions. A dilute aluminium alloy (Al-1 wt. % Zn-0.2 wt. % In-0.1 wt. % Sn) has been produced which can be sprayed to give sacrificial protection to high strength aluminium alloys which are susceptible to stress corrosion cracking.

Coating Methods

There have been notable improvements in the control, efficiency and understanding of several of the coating processes.

Spray Coatings Advances have taken place in arc spraying to promote faster rates of deposition and greater control over molten particle sizes. Improvements in substrate preparation have lessened the risk of the coating peeling in service. To seal coatings a specially formulated paint of low viscosity with inert polymer pigments has been developed. This sealant penetrates the pores and forms a surface film. The pore sealing treatment remains intact for long periods and maintenance is not required with the same frequency as was the case with conventional paint schemes.

Hot Dipped Coatings Major attempts have been made to improve the quality of aluminised steel strip. Requirements on coating thickness and uniformity have been imposed. It is the speed of sheet movement, length of path in the molten bath, temperature and composition of the bath that control the thickness of the intermetallic layer which lies below the aluminium outer surface. The process of intermetallic alloy formation is diffusion controlled, and it is usual that some dissolution of iron into the molten aluminium does occur at a rate, dc/dt , which is given by

$$\frac{dc}{dt} = \frac{KS}{V} (C_s - C_l) \quad (13.1)$$

where S is the surface area of the dissolving material, V is the solvent (aluminium) volume and K is a constant. The rate of dissolution is dependent on $(C_s - C_l)$, i.e. the difference between solubility limit of iron in aluminium and the concentration of iron in the bath at time, t . Problems can exist in maintaining constant bath conditions as throughput of sheet steel increases. Two coatings are available: type 1 (Al-9-11 wt. % silicon), and type 2 (unalloyed aluminium). Silicon almost doubles the solubility limit, C_s , of iron in aluminium and reduces the thickness of intermetallic, in the coating. Variations in the composition and structure of the intermetallic layer have been noted as silicon is added to the alloy. In the unalloyed aluminium case the coating is mainly Fe_2Al_3 , whilst in a 11 wt. % Si alloy the intermetallic compounds $FeAl_3$, Fe_2SiAl_8 and Fe_3SiAl_{12} all become possible.

BS 6536:1985 refers to four grades of carbon steel strip coated with Al-Si alloys containing 5-11 wt. % Si. The availability of the steel grades allows account to be taken of the type and degree of forming which is to be applied to the coated steel. Various coating masses are supplied in the range 40-180 g/m² which may be additionally protected by a chromate passivation treatment.

Much interest has developed in 'Galvalume', a product of the Bethlehem Steel Corporation in the USA. This is produced from a bath of composition Al-43 wt. % Zn-1.6 wt. % Si. It is claimed that this coating provides better galvanic protection to steel than aluminium. BS 6830:1987 refers to continuously hot-dipped aluminium-zinc alloy coated steel flat products. The standard does not specify the composition of the coating, but lists six steel grades which may be used at various strength levels with different degrees of formability. Coating masses are available at 150 and 185 g/m².

Calorised Coatings The nickel- and cobalt-base superalloys of gas turbine blades, which operate at high temperatures, have been protected by coatings produced by cementation. Without such protection, the presence of sulphur and vanadium from the fuel and chloride from flying over the sea promotes conditions that remove the protective oxides from these superalloys. Pack cementation with powdered aluminium produces nickel or cobalt aluminides on the surfaces of the blade aerofoils. The need for overlay coatings containing yttrium have been necessary in recent times to deal with more aggressive hot corrosion conditions.

Vacuum Deposited Coatings Aluminium coatings have been strongly considered as a replacement for cadmium in the protection of high-tensile steel

and titanium parts. Ion vapour deposition ('Ivadising') produces coatings in the thickness range 7.5–25 μm . Such coatings are often chromated to produce better surfaces for subsequent painting. In 5% salt spray the coatings are inferior to cadmium, but if SO_2 is introduced into the salt spray the aluminium coating shows the greater resistance. Developments in production equipment have taken place which allow large parts to be coated, whilst barrel coaters are used for fasteners and small components.

Electroplating Again the replacement of cadmium has been the driving force for the development of the 'Siemens Process' which uses an aluminium alkyl complex together with sodium fluoride in a toluene solution. This bath is capable of producing a 10–20 $\mu\text{m}/\text{h}$ plating rate under a nitrogen gas atmosphere. Problems of hydrogen evolution and the embrittlement of high strength steels is minimised. Adhesion is not as good on titanium and aluminium alloys as on steel substrates. A wide range of corrosion tests have demonstrated that aluminium coatings in the thickness range 5–100 μm are the equal of cadmium. The coatings may also be anodised or chromated.

Corrosion Resistance

Tests (to ASTM G-1-72) in industrial and marine atmospheres over periods of five years on Type 2 unalloyed coatings produced on steel by hot dipping have demonstrated differences in corrosion performance. In the more aggressive industrial atmosphere the corrosion rate of the ground side of the sheet is faster initially but then slows down. In the marine atmosphere the rate is slow initially but in the later stages of exposure the corrosion rate does not fall. 'At relative humidity values >70% the presence of moisture encourages the reactions $\text{SO}_2 \rightarrow \text{SO}_3 \rightarrow$ sulphuric acid and oxide film breakdown occurs. A new film of sulphate plus hydrated oxide eventually stifles corrosion reactions in the industrial atmosphere. Longer term tests in a marine atmosphere (15 years) can cause perforation of the coated sheet from the ground-facing side. This is explained in terms of longer periods of wetness and the greater propensity to retain salt on that side. A more constant corrosion rate results from the presence of a high-conductivity film with sea-salt incorporated.

Aluminised steel produced by hot dipping is used in the construction of parts of many exhaust systems of road vehicles. Failure of some of these exhausts does take place well within the expected two-year average life. This arises in the rear end of the exhaust where dew point corrosion occurs on the inside of the system. 'Acid dew' of pH 2.7–3.1 is produced in the exhaust gases at temperatures below 48°C and this concentrates as the system eventually heats up towards 100°C. The aluminised coating is attacked at weak positions, e.g. where holes have been punched and the aluminium does not completely coat the steel. Eventually, the aluminium coating is undermined and the steel severely attacked. It is estimated that the use of aluminium coatings can increase the life of unprotected steel by at least 12%.

Aluminium does provide a protective barrier to corrosive attack on steel but its ability to provide sacrificial protection is limited. The use of Al-Zn

hot-dipped coatings does result in greater sacrificial action. It is claimed that such action is gained without too much loss on the general corrosive attack on aluminium. This has promoted the use of Al-Zn coatings on steel roofing panels, and exposure tests to date point towards very good service in this field. With the recently discovered Al-Zn-In-Sn alloys, sacrificial protection is dependent on the indium content.

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13.3 Cadmium Coatings

In some environments cadmium gives better protection than zinc (Section 13.4); it is, however, considerably more costly. It does not compete with zinc on articles on which a high degree of protection can be achieved by the use of a thick film deposited by hot dipping (immersion in molten zinc, i.e. galvanising) or metal spraying. Where only thin coatings of 25 μm or less are tolerable, the greater protection of cadmium in some environments is worth while, and as uniform thin coatings must be deposited by relatively expensive processes such as electroplating, the greater cost of cadmium then has little effect on the cost of the finished article. However, because of the toxic nature of both the metal and its compounds, the use of cadmium is generally limited to those applications that demand the unique combination of properties that cadmium possesses.

Nature and Degree of Protection

Coatings of both cadmium and zinc protect steel mainly by simple physical exclusion. At gaps in the coating, however, whether these are in the form of porosity, pits, scratches or cut edges, protection is by sacrificial action of the coating followed probably by the plugging of gaps with sparingly soluble corrosion product.

It is not at once clear why cadmium should be sacrificially protective to steel. Standard equilibrium electrode potentials of iron and cadmium in contact with solutions of their salts of normal activity, given in Table 13.3, suggest that iron should be sacrificial to cadmium, but Hoar¹ has shown by means of E/I curves that the mixed potential of corroding cadmium will be more electronegative than the mixed potential of corroding iron. This follows from the higher exchange current for $\text{Cd} \rightarrow \text{Cd}^{2+} + 2e$. Under these circumstances iron will be sacrificially protected by cadmium (see also Section 1.4). Whatever the explanation, the fact of sacrificial protection is reflected in the potentials, also given in Table 13.3, found for the two metals in sea-water.

The degree of protection given in practice by zinc and cadmium, whether by physical exclusion or by sacrificial action at gaps, depends on the durability of the coatings themselves against corrosive attack. It is now well established that, thickness for thickness, cadmium is more resistant to

Table 13.3 Potentials of iron, cadmium and zinc

<i>Metal</i>	<i>Standard electrode potential, hydrogen scale (V)</i>	<i>Corrosion potential* in flowing sea-water, hydrogen scale (V)</i>
Iron	-0.44	-0.36
Cadmium	-0.40	-0.45
Zinc	-0.76	-0.76

* The corrosion potential will vary with aeration and velocity of the sea-water.

Table 13.4 Corrosion rates of zinc and cadmium coatings in various atmospheres

<i>Location</i>	<i>Rate of corrosion of electrodeposited coating (μm/y)</i>	
	<i>Zinc</i>	<i>Cadmium</i>
Industrial	5.1	10.2
Suburban	1.8	2.3
Marine	2.5	1.3

marine and tropical atmospheres and zinc more resistant to industrial atmospheres. This is well demonstrated by comparative tests made by Biestek² in various laboratory conditions, and by Clarke and Longhurst³ in practical tropical exposure tests. Table 13.4 gives the order of corrosion rates, based on the results of these and other⁴ tests. It must be emphasised that these figures give only a broad comparison; actual corrosion rates will be much affected by the exact environment.

If the corrosion mechanism in an industrial atmosphere is mainly a straight chemical dissolution in sulphur acids, then the relative chemical equivalents present in a given thickness of the two metals account for a large part of the difference in corrosion rate. In an unpolluted humid atmosphere the slightly greater corrosion resistance of cadmium compared with zinc at unit thickness (and therefore much greater resistance per unit chemical equivalent) is likely to be due to a greater insolubility and protective power of the first corrosion product. The solubility data in Table 13.5 (quoted from the *Handbook of Chemistry and Physics*, 40th edition) show that cadmium hydroxide is more soluble in water than zinc hydroxide, but that the cadmium carbonate is the less soluble, it is concluded therefore that the protective films formed are carbonates or possibly basic carbonates. The considerably greater comparative corrosion resistance of cadmium in a marine atmosphere must be postulated as being due to a greater insolubility of the basic chloride of cadmium compared with that of zinc.

In conclusion, relative cost and relative behaviour towards different conditions of exposure lead to the use of zinc on parts on which thick films can be tolerated and for general industrial use, and of cadmium for fine-tolerance special applications, such as aircraft and instrument parts, required to withstand conditions include humid and marine atmospheres.

Table 13.5 Solubility in water of cadmium and zinc carbonates and hydroxides

<i>Metal</i>	<i>Solubility (g/100 ml)</i>	
	<i>Carbonate</i>	<i>Hydroxide</i>
Cadmium	insoluble	0.000 26
Zinc	0.001	0.000 000 26

Other Factors Governing the Choice between Zinc and Cadmium

As well as the reasons already given, other considerations influence the choice between zinc and cadmium.

Cadmium is easier to solder and has a lower contact resistance than zinc, and for such reasons it may be selected for certain applications. However, account must be taken of the toxic nature of cadmium and cadmium vapour.

On very strong steels cadmium is also preferred because it appears that cadmium electroplating from a given type of electroplating solution, e.g. a specially formulated cyanide solution, causes less hydrogen embrittlement than zinc plating from the same type of solution⁵. On the other hand, on steels subject to elevated temperatures in use, the possibility of intergranular penetration of stressed steel which occurs above (and even, if the steel is highly stressed, somewhat below) the melting point of the coating, may lead to the choice of zinc (m.p. 419.5°C) in preference to cadmium (m.p. 321°C).

Acid vapours emitted by wood, oleoresinous paints and some plastics (cf. Section 18.8-10) attack both zinc and cadmium. The relative behaviour varies, and appears to depend on the nature and concentration of the acid vapours and on the relative humidity. For these conditions of exposure, therefore, no advice can be given as to which metal should be used. It should not be assumed, therefore, that because one metal has failed therefore the other would be better.

Both metals are applied to copper-base alloys, stainless steels and titanium to stop bimetallic corrosion at contacts between these metals and aluminium and magnesium alloys, and their application to non-stainless steel can serve this purpose as well as protecting the steel. In spite of their different potentials, zinc and cadmium appear to be equally effective for this purpose⁶, even for contacts with magnesium alloys⁷. Choice between the two metals will therefore be made on the other grounds previously discussed.

Protection of Cadmium Coatings

Full chromate passivation (Section 15.3) improves the corrosion resistance of both zinc and cadmium towards all environments and is applied for a wide range of applications. Clear and olive-coloured chromate coatings can also be applied for certain purposes. The highest degrees of corrosion protection

are generally obtained from olive-coloured chromate coatings. Passivation improves the adhesion of normal types of priming paints, but for best adhesion and protection an etch primer should be used.

Methods of Deposition

Electroplating Cadmium is usually electroplated from a cyanide solution. Zinc is also deposited from cyanide electrolyte, but for some applications mildly acidic and alkaline non-cyanide electrolytes are increasingly being used. Typical cyanide-based electrolyte formulations for both metals taken from Specifications DTD 903 and 904 are given in Table 13.6.

Table 13.6 Typical plating solutions for zinc and cadmium

Solution	Constituents				
	Zn or Cd (as metal) (min-max) (g/l)	Total cyanide (as NaCN) (min-max) (g/l)	Caustic soda (min-max) (g/l)	Temperature of operation (min-max) (°C)	Current density (A/dm ²)
Zinc plating*	25-50	56-112	40-80	32 (optimum)	1-2 (vat) 0.3-0.7 (barrel)
Cadmium plating					
Vat	14-17	56-63	11-14	15-35	1.0
Barrel	23-27	78-84	17-20	15-35	1.0

*For barrel plating, solution concentrations towards the maximum are recommended. It is also important to maintain the constituents in the ratios recommended in the specifications.

Other solutions, some based on cyanide, some on sulphate, fluoborate, etc. will be found in textbooks and handbooks of electroplating, and a comprehensive review of methods and of their relative advantages has been published by Such⁸. Much work has been devoted to the development of cadmium plating processes which cause little or no hydrogen embrittlement to very strong steels; references are given in Section 8.4 and in a paper by Yaniv and Shreir⁹. However, hydrogen removal can be effected by baking the steel at 200°C after plating.

Vapour deposition Hydrogen embrittlement can be avoided by depositing cadmium by vacuum evaporation. Vapour plating is carried out in a chamber evacuated to below 2.7×10^{-3} N/m². Cadmium metal is placed in mild-steel boats arranged along the chamber and heated to about 200°C. The evaporating metal moves in straight lines, so the parts to be coated are held in jigs that rotate on their own axes and revolve round the chamber, thus presenting all surfaces to the moving vapour. Before evaporation is begun, the parts must be cleaned by ion bombardment in a high-tension (≈ 1 kV) glow discharge at a pressure of approx. 4 N/m². Formerly, the glow discharge was stopped before the chamber was pumped down to evaporation pressure, but adhesion of the coating was poor unless the parts had first been roughened by fine abrasive blasting. In an improved process¹⁰ the glow discharge is maintained concurrently with pumping down and the start of evaporation; under these conditions there is no interval during which oxide

reforms on the steel by reaction with residual oxygen in the chamber, cadmium atoms arrive on a surface still under bombardment, and adhesion of the coating is good even on smooth machined surfaces.

Specifications for Cadmium Plating

Cadmium plating for general engineering use is covered by BS 1706:1960 and BS 3382: 1961, and for aircraft parts by Ministry of Aviation Supply Specification DTD 904. Special requirements for very strong steels are given in Defence Standard 03-4 (Directorate of Standardisation, Ministry of Defence).

Health and Safety Cadmium metal and its compounds are toxic and are injurious to health, and for this reason, cadmium is being replaced by other forms of coating wherever possible. For a number of important applications, however, no suitable alternatives have yet been identified. Where cadmium plating continues to be used, it is essential to comply with the regulations covering the use of cadmium.

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13.4 Zinc Coatings

It is estimated that approximately 40% of the world production of zinc is consumed in hot-dip galvanising of iron and steel, and this adequately demonstrates the world-wide use of zinc as a protective coating. The success of zinc can be largely attributed to ease of application, low cost and high corrosion resistance.

Methods of Application

The principal method for applying zinc coatings to iron and steel is hot-dip galvanising. There are four other important methods, each of which has its own particular applications; these methods are spraying, plating, sherardising and painting with zinc-rich paints. The choice of method in any given case is determined by the application envisaged, and the five processes may be said to be complementary rather than competitive, for there is usually little doubt as to which is the best for any particular purpose. Processes of applying coatings by various methods are discussed in detail elsewhere¹ and are considered in Chapter 12, and will not, therefore be considered here. The reactions inherent in galvanising tend to ensure a thick and even coating but guides to the inspection of galvanising, sherardising and zinc spraying are available².

Characteristics of Zinc Coatings

In practice the thickest zinc coatings can be obtained by hot-dip galvanising or spraying. Table 13.7 compares the essential aspects of each coating. Plated coatings can also be produced mechanically in a wide range of thicknesses as well as electrochemically.

The thickness of hot-dip galvanised coatings depends on the nature of the steel and the dipping conditions. It can be controlled to a certain extent in practice. Heavier coatings are obtained on grit-blasted steel or on steels of high silicon content, and at higher operating temperatures and longer dipping times. In strip galvanising, aluminium is deliberately added to the bath to suppress the action between molten zinc and steel, with the result that lighter coatings are produced compared with those on fabricated assemblies galvanised after manufacture. Mechanical wiping of the surface on withdrawal from the bath, as employed in wire or sheet galvanising, also causes a reduction of coating thickness.

Table 13.7 Comparison of zinc coatings

Characteristics of coating	Hot-dip galvanising	Metal spraying	Plating	Sherardising	Zinc dust painting
1. Process considerations	Parts up to 20 m long and fabrications of 18 m × 2 m × 5 m can be treated. Care required at design stage for best results. Continuous galvanised wire and strip up to 1.4 m wide) in UK	No size or shape limitations. Access difficulties may limit its application, e.g. inside of tubes. Best method for applying very thick coatings. Little heating of the steel	Size of bath available. Process normally used for simple, fairly small components suitable for barrel plating or for continuous sheet and wire. No heating involved	Batch processing is mainly suitable for fairly small complex components. Semi-continuous process for rods, etc.	Can be brush, spray or dip applied on site when necessary. No heating involved. Performance varies with media used
2. Economics	Generally the most economic method of applying metallic zinc coatings 20–200 μm thick	Most economic for work with high weight to area ratio. Uneconomic on open mesh	Used, where a very thin zinc coating is sufficient. Thick coatings are expensive.	More expensive than galvanising for equivalent thicknesses. Generally used when control of tolerances is more important than thickness of coating	Low overheads but high labour element in total cost as with all paints. Thixotropic coatings reduce number of coats and hence labour costs
3. Adhesion	Process produces iron-zinc alloy layers, overcoated with zinc; thus coating integral with steel	Good mechanical interlocking provided the abrasive grit-blasting pretreatment is done correctly	Good, comparable with other electroplated coatings	Good—the diffused iron-zinc alloy coating provides a chemical bond	Good—abrasive grit blasting preparation of the steel gives best results
4. Thickness and uniformity	Normally about 75–125 μm on products, 25 μm on sheet. Coatings up to 250 μm on products by prior grit-blasting. Very uniform—any discontinuities due to poor preparation of the steel are readily visible as 'black spots'	Thickness variable at will, generally 100–200 μm but coatings up to 250 μm or more can be applied. Uniformity depends on operator skill. Coatings are porous but pores soon fill with zinc corrosion products; thereafter impermeable	Thickness variable at will generally 2–25 μm . Thicker layers are possible but generally uneconomic. Uniform coating within limitations of 'throwing power' of bath. Pores not a problem as exposed steel protected by adjacent zinc	Usually about 12–40 μm closely controlled. Thicker coatings also possible. Continuous and very uniform even on threaded and irregular parts	Up to 40 μm of paint (and more with special formulations) can be applied in one coat. Good uniformity—any pores fill with reaction products

Table 13.7—(continued)

<i>Characteristics of coating</i>	<i>Hot-dip galvanising</i>	<i>Metal spraying</i>	<i>Plating</i>	<i>Sherardising</i>	<i>Zinc dust painting</i>
5. Formability and joinability	Applied to finished articles, not formable: alloy layer is abrasion resistant but brittle. Sheet has little or no alloy and is readily formed. All coatings can be arc or resistance welded	When applied to finished articles, forming not required. Can weld through thin coating if necessary but preferable to mask edges to be welded and spray these afterwards	Electroplated steel has excellent formability and can be resistance spot welded. Small components are usually finished before electroplating or mechanical coating	Applied to finished articles: forming not required. Excellent abrasion resistance	Abrasion resistance better than conventional paints. Painted sheet can be formed and resistance welded with little damage
6. British standards	General work: BS 729 Continuous galvanised: plain sheet: BS 2989 Corrugated sheet: BS 3083 Wire: BS 443 Tubes: BS 1387	BS 2569: Part 1	BS 1706 Threaded components: BS 3382	BS 4921	BS 4652 for the paint
7. Extra treatments	Conversion coatings; chromates used to prevent storage stains on new sheet; chromates or phosphates used as base for paints or powder coatings. Weathered coatings painted for long service	Usually sealed; sealed surface is suitable base for paints on long-life structures. Alternatively sealer can be reapplied periodically	Conversion coatings, e.g. chromates used to prevent 'wet storage' stain. Chromates or phosphates used as a base for paints	Can be painted if required	Can be used alone, or as primer under other paints

Properties and Nature of the Coatings

The actual structure and composition of zinc coatings depends upon the method of deposition. Zinc coatings produced by hot-dip galvanising and sherardising consist partly or wholly of iron-zinc alloys. Sprayed and plated zinc coatings contain no alloys, plated coatings consisting essentially of pure zinc. The characteristic properties of each type of coating are discussed below.

Hot-dip galvanised coatings (see Section 12.2) Here the coating is not uniform in composition but is made up of layers of zinc-iron alloys becoming progressively richer in zinc towards the coating steel interface, so that the actual surface layer is composed of more or less pure zinc. Because of this alloy formation there is a strong bond between the coating and the steel. The alloy layers are harder than mild steel.

The nature and thickness of the alloy layers are influenced greatly by the composition of the underlying steel, and also by the galvanising conditions. Notably the presence of silicon in the steel encourages the formation of iron-zinc alloys and thereby leads to the formation of heavier coatings, and indeed a steel with a high silicon content is often used intentionally when very heavy zinc coatings are required. In such cases the coating may consist entirely of iron-zinc alloys, and this is seen in the uniform grey spangle-free appearance of the galvanised surface obtained under these conditions.

The addition of up to 0.2% of aluminium to the galvanising bath, on the other hand, depresses the formation of alloys and produces lighter and more ductile coatings, which are more suitable for galvanised sheet since they render it more amenable to bending and forming.

Sprayed zinc coatings Details of the method and the nature of the coatings are given in Section 12.4. In this method there is no alloy formation and the bond is primarily mechanical. Although porous, the coating is protective partly due to its sacrificial action and partly due to the zinc corrosion products which soon block up the pores, stifling further attack.

Zinc plating Electroplating with zinc normally gives a dull-grey matt finish, but lustrous deposits can be obtained by adding brighteners to the electrolyte. Mechanical coating also gives a dull finish. The coating is of uniform composition throughout, containing no alloy layer, (Section 12.1). Plated coatings are very ductile and zinc-plated sheet can therefore be readily fabricated. Mechanical deposition of zinc by barrel-plating is also possible for small parts.

Sherardising This is another alloy-forming process, a typical coating containing alloys with 8 or 9% of iron. Like galvanised coatings, the deposits are very hard (Section 12.3).

Relative Advantages of the Coating Methods

Each coating method has its own particular advantages, which are really the decisive factors in determining which one is used for a given purpose. Consideration must be given to the complexity and size of the work, the corrosion resistance, and hence the coating thickness needed, and the quality of finish required.

Hot-dip galvanising produces a thick coating which thoroughly covers the work, sealing all edges, rivets, seams and welds when fabricated articles are treated. The size of the article which can be treated is limited to a certain extent by the size of the galvanising tank, but the technique of double dipping, i.e. dipping first one end and then the other, makes it possible to treat surprisingly large items, over 20 m long, successfully. Hot-dip galvanising is the most widely used method for coating with zinc.

Zinc spraying possesses the important advantage that, since the equipment is essentially portable, it can be applied on site to either small or large structures. Thick coatings can be applied where desired, and it is possible to ensure that welds, edges, seams and rivets on finished articles receive sufficient coverage. It is not normally a suitable process for coating the inside of cavities or for coating open structures, such as wire meshes, since a large amount of zinc would be wasted. In hand spraying the uniformity of the coating depends largely on the skill of the operator.

Zinc coatings produced by plating have the advantages that the thickness can be accurately controlled according to the protection desired.

The acid zinc sulphate bath is used for applying coatings to uniform sections, e.g. box strapping, wire, strip, etc. The plating rates; in these solutions can be very high. The throwing power of this bath is poor, and for more intricate shapes and where appearance is important the cyanide bath is preferred. Bright deposits can be produced from the latter by the use of either addition agents or bright dips.

Sherardising is distinguished particularly by the uniformity of the coatings which it produces. This makes it an ideal process for work, such as screw threads, where close tolerances are required and where complex or recessed parts are involved, since the inside surfaces of pipes and other hollow articles receive coatings comparable with those on the outside. The coating is very hard and offers a high resistance to abrasion. The maximum size of the articles which can be sherardised is limited by the size of the drums. In general, sherardising is best suited to the treatment of small castings, forgings and pressings, and fixings, such as wood screws, nuts, bolts, washers, chains, springs, etc.

The outstanding virtue of zinc-rich paints is simplicity in application. No special equipment is required and the operation can, of course, be carried out on site, large or small structures being equally suitable for treatment. While there is some evidence that the zinc-rich paints will reduce iron oxides remaining on the steel surface, proper surface preparation is as important here as with traditional paints if the best results are to be achieved. The main use of zinc-rich paints is to protect structural steel-work, ships' hulls, and vulnerable parts of car bodies, and to repair damage to other zinc coatings.

Corrosion Resistance of Zinc Coatings

There are two main reasons why zinc is chosen as a protective coating for iron and steel. The first is the natural resistance of zinc itself against corrosion in most atmospheric conditions, and the second is the fact that zinc is electronegative to iron and can protect it sacrificially*.

*The reversal of polarity of Zn and Fe which can occur in certain circumstances is discussed in Section 1.3.

The corrosion resistance of zinc is discussed in Section 4.7, and it is only necessary here to say that zinc is protected against further attack by a film of corrosion products. It is remarkably resistant to atmospheric corrosion except perhaps in the most heavily contaminated industrial areas, and even there its use as a protective coating is still a sound practical and economic proposition. The value of zinc coatings as a basis for painting under very aggressive conditions has been clearly demonstrated.

The natural corrosion resistance of zinc is, therefore, its most important property in relation to zinc coatings. The electrochemical property becomes important when the zinc coating is damaged in any way to expose the steel, when sacrificial corrosion of the zinc occurs and the steel is thereby protected. Moreover, the corrosion product of the zinc normally fills the break in the coating and prevents or retards further corrosion of the exposed steel.

Life of Zinc Coatings in the Atmosphere

As the protective value of the zinc coating depends largely on the corrosion resistance of zinc, the life of a coating is governed almost entirely by its thickness and by the severity of the corrosive conditions to which it is exposed. Extensive tests and field trials which have been carried out have shown that the life of a zinc coating is roughly proportional to its thickness in any particular environment³ and is independent of the method of application.

The corrosion rates and lives of zinc coatings in UK atmospheres are given in Table 13.8. These are based on practical experience as well as exposure trials. The figures should be taken only as a guide because of the difficulty of defining atmospheres in a word or two (indeed there is now a tendency for research workers to define the corrosivity of an atmosphere in terms of the corrosion rate of zinc) because of unpredictable local variations from place to place and time to time. For example, moorland which is frequently covered with acid-laden mist can be very corrosive.

Corrosion tests have also shown that there is a difference in the rates of corrosion throughout the year. This is partly because the sulphur content of the air is greater in winter than summer and partly because more of the

Table 13.8 Typical corrosion rates and lives of zinc coatings in the UK

Atmosphere	Corrosion rate		Life of coating with average thickness (years) ¹			
	gm ⁻² y ⁻¹	µm y ⁻¹	200 µm*	100 µm†	25 µm‡	5 µm§
Rural	14	2	50-150	25-75	6-20	1-3
Urban	40	5	30-50	15-25	4-6	≈ 1
Marine	40	5	30-50	15-25	4-6	≈ 1
Industrial	80	10	10-30	5-15	1-4	0.25-1

* Can be produced either by grit-blasting before galvanising or by zinc spraying.

† Typical thickness of coating on galvanised or zinc-sprayed structural steel.

‡ Typical thickness of coating on galvanised sheet or sherardised components.

§ Typical thickness of zinc plating.

¹ The lives given are additional to the life of the unprotected steel.

zinc corrosion products are dissolved under the wetter winter conditions. Thus if unpainted zinc coatings are first exposed to the atmosphere in spring or early summer a more protective film will be formed.

Detailed test results for a 2-year exposure period⁴ are given in Table 13.9. It should be remembered that test sites are sometimes chosen because they are believed to represent particularly corrosive examples of the type of atmosphere being studied. The ratios of steel: zinc losses are particularly interesting. It shows that zinc is far less affected than steel by many chloride-containing atmospheres. Time of wetness and amount of atmospheric SO_2^{13} are the most important factors with Zn. On a global view the single word description of the site is often misleading; particularly, it gives no indication of the times each year that objects remain wet, which varies considerably from country to country and also within countries.

An extensive compilation of atmospheric exposure test data on zinc is now available⁵ and complements the slightly earlier critical study by Schikorr⁶.

Water Zinc-coated steel, like zinc, behaves less favourably in distilled and soft waters than in hard waters, where the scale-forming ability of the hardness salts provides considerable protection. Hot-dip galvanised tanks, cisterns and pipes are very widely used for storing and carrying domestic water supplies throughout the world, and as a rule such equipment gives long and trouble-free service (Section 9.3) and is hygienically acceptable.

Sea-water The protective properties of zinc coatings in sea-water have been shown to be very good, and zinc is widely used as a coating metal in the shipbuilding industry and for protecting structural steel work on docks and piers, etc. In BISRA tests at Gosport⁷, specimens of steel coated with aluminium, cadmium, lead, tin and zinc were immersed for two years. In this time all but the zinc-coated specimens had failed. The zinc-coated specimens were then transferred to Emsworth and immersed for a further four years—a total of six years—before the coatings ceased to give complete protection. The coating on these specimens was about 900 g/m^2 , indicating a rate of attack of about $20 \mu\text{m/y}$ in this sea-water. Other tests^{3,8} show corrosion rates of $10\text{--}25 \mu\text{m}$.

Conditions within a few hundred metres of the surf line on beaches are intermediate between total immersion in sea-water and normal exposure to a marine atmosphere. High corrosion rates can occur on some tropical surf beaches where the metal remains wet and where inhibiting magnesium salts are not present in the sea-water.

Soil Galvanised pipe is frequently used for underground water services. Table 13.10 gives results of tests⁹ carried out with galvanised pipes and plates buried at different sites.

The specimens were removed after five years, when the only ones that had failed were some plates buried in made-up ground, consisting of ashes, at Corby and one pipe at Benfleet. At Corby no galvanised pipes were exposed and most of the coatings on the plates had corroded away. For this reason no figures are recorded for Corby in Table 13.10. The high rate of corrosion at Benfleet was attributed to the fact that the specimens were below the soil-water level for about half their life as the tide rose and fell.

Similar tests have been carried out in the United States¹⁰; in these the

Table 13.9 Average loss of zinc in two years and steel/zinc ratio for 45 test sites⁴

<i>Location</i>	<i>Described by authors as:</i>	<i>2-year test: zinc lost per year (μm)</i>	<i>Steel/zinc loss ratio (by weight)</i>	<i>Life of 100 μm zinc coating (calc.) without maintenance (years)</i>
Norman Wells, N.W.T., Canada	Rural	0.2	10.3	500
Phoenix, Ariz., USA	Rural	0.3	17.0	300
Saskatoon, Sask., Canada	Rural	0.3	21.0	300
Esquimalt, Vancouver Is., Canada	Rural/ marine	0.5	31.0	200
Fort Amador Pier, Panama C.Z.	Marine	0.7	25.2	150
Melbourne, Aust.	Industrial	0.8	37.4	125
Ottawa, Canada	Urban	1.1	19.5	90
Miraflores, Panama C.Z.	Marine	1.2	41.8	80
Cape Kennedy, 0.8 km from ocean, USA	Marine	1.2	84.0	80
State College, Pa., USA	Rural	1.2	22.0	80
Morenci, Mich., USA	Rural	1.2	18.0	80
Middletown, Ohio, USA	Semi- industrial	1.3	26.0	75
Potter County, Pa., USA	Rural	1.3	18.3	75
Bethlehem, Pa., USA	Industrial	1.3	32.4	75
Detroit, Mich., USA	Industrial	1.4	12.2	70
Manila, Philippine Is.	Marine	1.5	39.8	65
Point Reyes, Calif., USA	Marine	1.6	364.0	60
Halifax (York Redoubt) N.S., Canada	Urban	1.6	18.5	60
Durham, N.H., USA	Rural	1.6	19.0	60
Trail, B.C., Canada	Industrial	1.6	24.2	60
South Bend, Pa., USA	Semi-rural	1.8	20.8	55
East Chicago, Ind., USA	Industrial	1.8	52.1	55
Brazos River, Texas, USA	Industrial/ marine	1.9	56.0	50
Monroeville, Pa., USA	Semi- industrial	2.0	28.4	50
Daytona Beach, Fla., USA	Marine	2.1	164.0	45
Kure Beach, N.C. 240-m lot, USA	Marine	2.1	80.0	45
Columbus, Ohio	Urban	2.2	16.8	45
Montreal, P.Q., Canada	Urban	2.5	10.9	40
Pilsea Island, Hants., UK	Industrial/ marine	2.5	21.6	40
Waterbury, Conn., USA	Industrial	2.6	9.8	40
Pittsburgh, Pa., USA	Industrial	2.7	13.1	35
Limon Bay, Panama C.Z.	Marine	2.7	25.9	35
Cleveland, Ohio, USA	Industrial	2.8	15.7	35
Dungeness, UK	Marine	3.7	148.0	27
Newark, N.J., USA	Industrial	3.8	15.1	25
Cape Kennedy, 55 m from ocean 9 m up, USA	Marine	4.1	45.5	24
ditto, ground level	Marine	4.3	117.0	23
ditto, 18 m up	Marine	4.5	33.0	22
Bayonne, N.J., USA	Industrial	4.9	17.9	20
Battersea, UK	Industrial	5.8	20.0	17
Kure Beach, N.C., 24 m lot, USA	Marine	6.5	93.0	15
London (Stratford), UK	Industrial	7.1	17.8	14
Halifax (Federal Bldg.), N. S., Canada	Industrial	7.6	17.0	13
Widnes, UK	Industrial	10.5	39.0	9
Galeta Point Beach, Panama C.Z.	Marine	15.9	49.4	6

Table 13.10 Loss of coating thickness of galvanised specimens after five years in various soils

<i>Location</i>	<i>Soil conditions</i>	<i>Galvanised pipes</i>		<i>Galvanised plates</i>		<i>Uncoated steel loss in thickness (μm)</i>
		<i>Initial thickness of coating (μm)</i>	<i>Loss of coating thickness (μm)</i>	<i>Initial thickness of coating (μm)</i>	<i>Loss of coating thickness (μm)</i>	
Benfleet	Alluvium or reclaimed salt marsh	82	47	90	52	200
Gotham	Keuper Marl (gypsum)	77	17	90	17	50
Pitsea	London clay	77	17	90	17	160
Rothamstead	Clay with glacial flints	82	13	95	13	120
Corby	Made up ground (ashes)	—	—	—	*	300

* Most of coating on plates corroded away.

maximum depth of pitting was also measured. Except in the most corrosive soils the maximum depth of pitting in steel specimens exposed for about $12\frac{1}{2}$ years was more than 11 times that in zinc-coated specimens, even though the ratio of the rates of corrosion was only about half that figure. This resistance to pitting, combined with the fact that rusting appears to start only when nearly all the zinc and zinc-iron alloys layers have corroded away, reduces the risk of premature failure in galvanised piping. The coatings on galvanised specimens remained virtually intact during exposure for $2\frac{1}{2}$ years in about half the 15 soils in which they were buried. Their corrosion resistance was most marked in alkaline soils. In clays and loams, where little or no organic material was present, a 600 g/m^2 coating could be expected to provide protection for 10 years or more.

Protective Systems Applied Subsequently to Zinc Coatings

Chromating Chromating is considered in Section 15.3. The chromate film on zinc is adherent and can be drab, yellow-green or colourless in appearance; the colour varies considerably with the method of application. It retards 'white rust', the white deposit which sometimes forms on fresh zinc surfaces which are kept under humid conditions (see Section 4.7). A chromate film is damaged by heat and if used as a basis for paint adhesion, should preferably not be heated above 70°C , nor for longer than 1 h.

Painting In mildly corrosive conditions zinc coatings will probably have a life longer than that expected of the coated article, and no further treatment of the coating will be necessary. When, however, the coating is subjected to a more strongly corrosive environment one or more coats of paint can, with advantage, be applied over the zinc.

Paint films used in conjunction with zinc coatings give systems whose lives are longer than the sum of the lives of the coatings used independently.

Paint applied to a suitably prepared zinc coating will last longer than would be the case if it were applied direct to iron or steel, and the need for repainting thus becomes less frequent. With hot-dip galvanised or zinc-plated coatings, however, it is necessary either to use special primers or to prepare the surface before painting. This is primarily because most oil-based paints react with the unprepared zinc surface to form zinc soaps resulting in poor adhesion.

Weathered galvanised steel surfaces give good adhesion for many paint systems, but where new galvanised or zinc-plated steel is painted or powder painted it is necessary to convert the surface into an adherent phosphate or chromate coating or to use specially developed primers¹¹. Many commercial phosphating processes are available, but all consist essentially of an etch in a phosphoric acid solution containing zinc salts and certain accelerators. These treatments produce uniform, fine-grained and strongly adherent phosphate films on the surface of the work. Many chromate finishes also give a satisfactory base for painting (see Section 15.3).

Etch primers are widely used. They are mostly based on polyvinyl butyral and contain chromates and phosphoric acid. They are said to act both as primers and as etching solutions because it is believed that the chromates and phosphoric acid form an inorganic film, which provides adhesion, while oxidised polyvinyl butyral provides an organic film. For direct application to new galvanised steel, the best known primers are based on calcium orthoplumbate pigment and metallic lead, but these are now less used for environmental reasons. Zinc-dust paints and zinc-phosphate pigmented paints are also used, but the trend is to use pretreatments to assure good adhesion.

Applications of Zinc Coatings

Zinc coatings are successfully used in a very wide field to protect iron and steel goods from corrosive attack.

The building trade is one of the largest users of zinc-coated steel. The frameworks of large modern buildings can be either galvanised or zinc-sprayed before erection, or sprayed on site. Where a framework is accessible, zinc-rich paints provide an excellent way of renovating old buildings. Apart from the structural aspect, galvanised sheeting is used for roofing, ventilation ducts and gutters, as well as for water tanks and cisterns, and galvanised pipe is used for public and domestic services.

In the Forth, Severn and many other suspension bridges, zinc coatings have an important function. The whole main structure is of steel and has been zinc-sprayed on the external surfaces, while the main cable and hanger ropes have been coated by continuous hot-dip galvanising. Case histories of galvanised multi-truss bridges cover more than 30 years.

Zinc-coated structures are used in pylons carrying electrical transmission lines, in masts for radio, television and radar aerials, and for supports for overhead wires on electrified railways.

An interesting new use of galvanised steel is for reinforcement of concrete. This reduces the risk of spalling and staining or can enable the depth of the concrete cover to be reduced leading to slimmer structures of lower cost.

Economics

All coatings cost money and a true appraisal of both the initial and maintenance costs is essential when specifying the protective scheme for a new structure. An example showing the comparative costs of galvanising and painting is given in Section 9.1.

Recent Developments

Since the previous edition was written, the main development has been the introduction of a range of zinc alloy coatings designed to give increased corrosion resistance and sometimes with additional advantages such as increased formability and retention of paint adhesion with a wider range of paints.

The zinc-aluminium alloys are most important. The zinc-55%-aluminium-1.5%-silicon alloy hot-dip coating was initiated over 20 years ago by the steel industry and has recently become of major worldwide importance (known as Galvalume, Zinalume, Alugalva, Aluzink, Aluzinc, Zinalit or Zalutite). The coating usually has 100-400% more corrosion resistance than galvanising in the atmosphere, but less cathodic protection and also has the inherent problem of aluminium alloys when in contact with alkalis.

Since 1980, the zinc-5%-aluminium (notably Galfan which has a mischmetal addition) alloys, which are essentially based on the eutectic structure, have been developed commercially. They give 30-200% increase in corrosion resistance in the atmosphere and are extremely flexible. They can be used for sheet, wire and some types of tube galvanising whereas the zinc-55%-aluminium alloy is restricted to sheet.

Intermediate alloy compositions include a zinc-15%-aluminium alloy for metal spraying (higher aluminium contents are unsuitable for spraying wire) and a zinc-30%-aluminium-0.2%-magnesium-0.2%-silicon coating (Lavegal) for sheet.

A further range of alloys has been produced using nickel. The 13% nickel alloy has been adopted commercially in the USA for electroplating sheet destined for car-body manufacture. Other developments range from 5 to 14% nickel. Additions at a much lower level—less than 0.1% nickel in the operating bath—are used in the hot-dip galvanising of products to give more uniform growth of the iron-zinc alloy layers than would otherwise occur on steels containing silicon.

Other alloy additions in commercial use include; iron (often a two-layer electroplated coating with less iron—typically 20%—in the under-layer to assist formability and more iron—often 80%—in the outer layer to assist paintability); cobalt (0.15-0.35%); similar amounts of chromium (the zinc/chromium/chromium-oxide coating known as Zincrox); and a range of ternary alloys and of composite coatings.

New coating techniques in commercial use are mechanical coating (now incorporated under 'plating' in Table 13.7) and adhesive-bonded or vapour-deposited coatings, although each of these represents less than 1% of the zinc coatings used.

The mechanical coatings are primarily barrel processed on to parts up to about 150 mm long or 400 g mass. Adhesive bonding (with a conductive adhesive to maintain the electrochemical protection by zinc) is particularly suitable for wrapping pipes. Vapour deposition has some use in products but the newest development is application on continuous strip for car-body manufacture—the surface is smooth so that the subsequently painted surface has no unevenness.

Duplex coatings of zinc followed by organic materials have increased and there has been a swing away from lead-bearing paints. One or two organic coats are sufficient. Some paints are formulated for direct application to zinc surfaces, but adhesion is most assured by pretreatment with phosphate-type solutions, particularly as most paints are not covered by national specifications and slight modifications in formulation or method of application which may not be significant on steel can markedly affect adhesion, especially on untreated zinc surfaces. Sprayed powder coatings (see BS 6497) are applied over zinc for long-life decorative effects. Sprayed zinc coatings are often only sealed, i.e. a labile solution fills the pores in the coatings but provides no specified overlay.

Zinc or zinc-alloy coatings, previously used on luxury cars, are now being used on more mass-produced cars to meet 10-year warranties against perforation corrosion. In general, the percentage of steel which is zinc-coated is increasing. Hot-dip galvanising after fabrication, in addition to giving long lives to first maintenance, enables hidden interior areas of tubular space frames and lamp posts to be safely protected against failure by rusting. A new use is for earth reinforcement in which galvanised tie-bars, embedded deeply into prepared earth walls, hold in position concrete slabs forming the near-vertical exterior of road and rail embankments.

The bibliography covers some of the major developments.

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13.5 Tin and Tin Alloy Coatings

Tin Coatings

Methods of application (Chapter 12) Tin coatings are applied by hot-dipping, electrodeposition, spraying and chemical replacement. A variant of hot-dipping called *wiping*, in which the tin is applied either solid or melted to the fluxed and heated surface and is wiped over it, is also used for local application, e.g. to one face of a sheet or vessel. The hot-dipped and wiped coatings are bright; electrodeposited coatings may be matt or bright.

The electrolytes used for electrodeposition of matt coatings¹ for general purposes are: (a) an alkaline bath containing tin as stannate; (b) an acid bath containing stannous sulphate, free sulphuric acid, cresol-sulphonic acid, gelatin and β naphthol; and (c) an acid fluoroborate-bath containing organic addition agents. For high-speed plating on rapidly moving strip in the production of tinplate, the baths used are the 'Ferrosan Bath' based on stannous sulphate and phenolsulphonic acid, the 'Halogen Bath' based on chloride and fluoride (both with appropriate addition agents) and to a lesser extent, the alkaline stannate bath and the acid fluoroborate bath.

Bright coatings are deposited from acid stannous sulphate baths containing combinations of organic addition agents. The electrodeposited matt coatings may be brightened by momentary fusion. This process of flow-brightening or flow-melting is achieved with most of the electrolytic tinplate production by conductive or inductive heating; for manufactured articles, it is usually carried out by immersion in a suitable hot oil².

The hot-dipped coatings³ are distinct from the others in having practical thickness limits and in possessing an inner layer of intermetallic compound, usually described as the *alloy layer*. The flow-melted electrodeposited coatings also have an alloy layer, which is somewhat thinner than that obtained in hot dipping.

Coatings of tin produced from tin-containing aqueous solutions by chemical replacement may be used to provide special surface properties such as appearance or low friction, but protect from corrosion only in non-aggressive environments. Copper and brass may be tinned in alkaline cyanide solutions or in acid solutions containing organic addition agents such as thiourea. Steel may be first coated with copper and then treated

as copper, or it may be tinned in acid tin salt solutions with or without contact with zinc. Aluminium alloys may be tinned by immersion in alkaline stannate solutions.

Articles of steel, copper or brass which require a thicker coating than is possible by chemical replacement, and which are difficult to tin by normal electrodeposition, may be coated by immersion in alkaline sodium stannate solution in contact with aluminium suitably placed to act as anode.

Thickness of tin coatings The thicknesses of the various types of tin coating are shown in Table 13.11.

Table 13.11 Thicknesses of tin coatings

Hot dipped	1.5–25 μm
Electrolytic tinplate	0.4–2 μm
Wiped coatings	1–12 μm
Electrodeposits other than tinplate	2.5–75 μm
Flow-melted electrodeposits	2.5–7.5 μm
Sprayed coatings	75–350 μm
Chemical replacement coatings	trace–2.5 μm

Properties of tin coatings When the choice of coating is not governed by the size and geometry of the article to be coated, it depends upon appearance, the thickness required, and the degree of porosity which can be tolerated. Bright coatings, as produced by hot dipping, flow-melting or bright electrodeposition, have the advantage of smoothness, good appearance and resistance to finger-marking. The presence of an alloy layer in hot-dipped and flow-melted coatings also confers some advantage in the making of soldered joints. On the other hand, with hot-dipped coatings it is rarely possible to ensure absence of coating porosity, whereas electrodeposition can build the coating up to the thickness, above 25 μm , at which pores are unlikely to penetrate the coating.

Sprayed coatings have structures in which fine pores thread tortuous paths through the deposit, and it is necessary to apply a coating thickness of about 350 μm if all these paths are to be closed. Scratch-brushing of the deposit, however, makes it possible to consolidate the surface and to achieve adequate continuity in thinner deposits, e.g. 200 μm .

Tin coatings are ductile and are able to contribute a lubricating effect in the deep drawing of steel. The presence of the thin alloy layer in flow-melted tinplate coatings does not impair this property appreciably but bright electrodeposited coatings may be less ductile than others.

Sometimes a spontaneous outgrowth of metal filaments about 1 μm diameter, commonly called *whiskers*, occurs on tin coatings in a time after application which may vary from days to several years. This growth does not affect the protective quality of coatings but the whiskers are able to short-circuit compact electronic equipment. The character of the substrate is influential and tin coatings on brass should always be undercoated, e.g. with nickel or copper. The introduction of some impurities, e.g. 1% lead, into the tin coating is some safeguard. Hot-dipped or flow-melted coatings are rarely affected⁴⁹.

Corrosion Resistance of Tin Coatings

General considerations Influential factors in the behaviour of tin coatings are the variation according to environment in the relative polarity of coating and substrate, the nature of any intermetallic compound layers formed between coating and substrate and the extremely low rate of corrosion of tin in alkaline and mildly acid media in the absence of cathode depolarisers. The depression of the corroding potential of tin, when the tin ion concentration in solution is reduced by the formation of complex ions, has been referred to previously (Section 4.6). Iron may also be complexed and the potential of iron is affected by the presence of tin ions in solution. The extent of the potential shifts⁴ depends on the complexing agents present, the solution concentration and pH. The electrochemical relationship of tin and iron is therefore a complicated one, but for practical purposes, tin can be regarded as being anodic to iron in contact with such products as fruit juices, meat and meat derivatives and milk, in solutions of citric, tartaric, oxalic and malic acids and their salts, and in alkaline solutions. In solutions of inorganic salts, natural waters or atmospheric water, tin is cathodic to iron.

Supplementary protection can be given to tin coatings either by passivation treatments or by organic finishes. Passivation in chromate solutions gives some protection to the steel exposed at the base of pores as well as to the tin coating (Section 15.3). Electrolytic tinplate is passivated on the production line by rapid passage through acid solutions, usually dichromate, with applied cathodic current. Similar treatments may be employed on other forms of tinned cathodic metal, and a process of immersion in hot alkaline chromate⁵, which combines cleaning and passivation, is useful for treating metal coated by oil or other contaminants in manufacturing operations.

Tinplate for containers and closures is often decorated by colour printing and protected by clear lacquers. No surface preparation is carried out and difficulties with wetting and adhesion, sometimes associated with the character of the oxide layers on the surface, are rare.

The corrosion of tinned steel

Atmospheric corrosion During full exposure to the weather, some rust at pores in the coating soon appears. In coatings of thicknesses less than about 5 μm the rust spreads out from the pores and in due course the whole surface becomes covered by rust. With thicker coatings, this spread of rust does not occur. In industrial atmospheres, penetration of the steel may cease, after a few weeks, the surface becoming covered by a growing grey layer of tin corrosion product with faint rust stains; tin coatings of upwards of 12 μm will outlast zinc coatings of comparable thickness^{6,7}. In marine atmospheres, however, attack at pores persists even with the thicker coatings and pits are formed.

In most of its uses, e.g. the external surfaces of tinplate cans, tinned steel has only to resist condensed moisture. In the absence of pollution of the atmosphere by unusually large amounts of sulphur dioxide or chlorides, or of several days of continuous wetting, tinned steel remains unruined; even the thin porous coatings on the common grades of tinplate remain bright and unmarked over the periods involved in the commercial handling and domestic storage of cans, and the domestic use of kitchenware. When

wetting persists for long periods, especially if pools of water collect, rusting at pores begins. This situation can easily arise in the holds of ships in transit through the tropics unless proper precautions are taken; shipment in large sealed containers seems likely to avoid most of the trouble⁸. The conditions needed to ensure complete absence of pore rust are similar to those needed to preserve uncoated steel, although with the tinned steel, rust-promoting conditions can be tolerated for a much longer period without the general appearance of the metal being spoilt.

Condensed moisture rarely produces serious pitting of the steel at pore sites, but for many purposes maintenance of appearance is important. The change in aspect which takes place on rusting is much influenced by the degree of porosity of the coating, which is usually dependent on coating thickness. The thinnest coatings of electrolytic tinplate of 5 g/m^2 of sheet (equivalent to a coating thickness of $0.4 \mu\text{m}$) will develop a continuous rust coating in conditions where a hot-dipped coating of 30 g/m^2 will show only inconspicuous rust spots. A coating heavier still may show no visible change.

The oil film present on both types of tinplate and on newly hot-dipped tinware has a slight protective value. The passivation processes have much more effect but this is unlikely to compensate for a substantial reduction in coating weight. The effects of oil and passivation on the outside of tinplate cans may be reduced during can manufacture, filling and sterilisation.

The resistance of tin to organic acid vapours emanating from wooden cases and from some insulating materials and paints gives tin an advantage over zinc and cadmium as a coating for equipment likely to be exposed to these vapours. There is, however, some risk of rust-spotting at pores in tin coatings; one method of trying to secure immunity of the coating from organic vapour corrosion and of the pores from rusting, consists in plating a layer of tin over a layer of cadmium or of zinc.

Immersion in aqueous media open to air Solutions in which tin is cathodic to steel cause corrosion at pores, with the possibility of serious pitting in electrolytes of high conductivity. Porous coatings may give satisfactory service when the corrosive medium deposits protective scale, as in hard waters, or when use is intermittent and is followed by cleaning, as for kitchen equipment, but otherwise coatings electrodeposited or sprayed to a sufficient thickness to be pore-free are usually required.

Sometimes it is possible to add corrosion inhibitors to an aqueous product that is to remain in contact with tinned steel. The normal inhibitors used for protecting steel, e.g. benzoate, nitrite, chromate, etc. are suitable, provided that they are compatible with the product and that the pH is not raised above 10. In a closed container with an air-space, such inhibitors will not protect the zone above the water-line, and possibly not the water-line zone itself, against condensate. Volatile inhibitors have been used to give protection to these areas.

Fruit juices, meat products, milk and milk products, fish and most vegetables, in which tin is likely to be anodic to steel, can be handled open to the air in tinned steel vessels. Some corrosion of the tin occurs at rates similar to those found for pure tin and in due course retinning may be necessary. The alloy layer in hot-dipped tin coatings is cathodic to both tin and steel and, under aerated conditions may stimulate the corrosion of both metals, but this effect appears to be unimportant in practice.

Tin is anodic to steel in alkaline solutions, the corrosion rate for a continuous coating being similar to that of pure tin, and tinned articles that are washed in aerated alkaline detergents slowly lose their coating.

Tinplate containers The behaviour of tinplate is basically similar to that of other types of tinned steel, but performance requirements of tinplate containers are special. Containers are used in several forms:

1. Cans with replaceable closures for such products as dry foodstuffs, pharmaceuticals, tobacco, solvents, liquid fuels and paint. These usually contain an appreciable amount of oxygen. Tinplate closures for bottles and jars made of non-metallic materials may also be considered in this category.
2. Sterilised sealed cans of foodstuffs, including fruit, vegetables, meat, fish and milk, which should contain only residual traces of oxygen.
3. Cans for beer and soft drinks.
4. Aerosol cans which may contain a propellant together with products such as paints, cleaners, cosmetic preparations and foodstuffs. These may also contain some oxygen.

With all of these containers, both the can and its contents must reach the user in a visibly good condition. Cans must therefore resist external rusting, and methods of achieving this (e.g. adequate coating thickness, passivation treatment, attention to packaging and storage conditions and, if need be, lacquering) have already been mentioned. In other respects, both the requirements and the methods of achieving them may differ for the several classes.

For categories 1 and 4, the relative polarity of tin and steel may be in either direction, depending on the product contained, but, more commonly, steel is anodic to tin and sufficient oxygen is present to make perforation by corrosion a possibility with water-containing products. Small quantities of water in nominally non-aqueous products can be seriously damaging because they are able to use all the oxygen present in the contents. Change of formulation, including addition of corrosion inhibitors, is possible for many non-food products and protection by lacquering is a generally available means of protection.

Containers of foodstuffs should not be unduly stained or etched and must not be perforated or allowed to become distended by pressure due to evolution of hydrogen, and the contents must not suffer unacceptable changes of colour or flavour. Long storage periods, e.g. two years, may be required.

Yellow-purple staining of can interiors may be produced by adherent films of tin sulphides formed by S^{2-} and HS^- compounds derived from proteins in meat and vegetable products. It may be prevented by suitable passivation treatment of the tinplate⁹ or by the use of appropriate lacquers. Loose iron sulphide, occasionally formed by sulphur-containing products at pHs above about 5.5 in the headspace of a can where there is some residual oxygen, is more objectionable and is not prevented by passivation or by normal lacquer since it occurs at breaks in the coating. Careful control of can-making and canning procedures is the best safeguard.

Discolouration of products inside cans may follow the reduction of colouring matters or the formation of new coloured compounds with tin or iron. This is a problem with strongly coloured fruits and the remedy is to

use fully lacquered cans. Other than this effect, dissolved tin has no objectionable action on the quality of canned products, but very small amounts of dissolved iron have adverse effects on flavour.

Except in special circumstances, the anodic relation of tin to steel and the inhibition of steel corrosion by dissolved tin¹⁰⁻¹² protects the unlacquered tinplate can of food from risk of perforation or from taking up appreciable quantities of iron. The main hazards are excessive dissolution of tin, which may impair the appearance of the can and breach food regulations, and evolution of hydrogen which may distend the can and make it an unsalable 'hydrogen swell'. The amount of hydrogen collecting in a can to produce a 'swell' is usually roughly proportional to the amount of iron dissolved, and the high rate of hydrogen evolution responsible for swells seems to arise from self-corrosion of the steel when protection by tin has been lost, and not from the combination of tin anode with steel cathode¹³.

In general, tin dissolution inside an unlacquered can has a high but diminishing initial rate followed by a steady slow rate¹⁴. The initial phase is associated with the reduction of cathodic depolarisers, including residual oxygen, and its duration and the corrosion rate reached depend on the nature of the product and on canning technology. In the second phase the cathode reaction is hydrogen ion reduction and the slow rate of tin dissolution, often equivalent to corrosion currents of the order of 10^{-9} A/cm², is due to the scarcity of effective cathodes. The area of steel exposed at pores and scratches may be expected to have some influence on the corrosion rate, and small grain size of the tin coating has been considered to be associated with high rates.

Many compounds capable of acting as cathodic depolarisers are naturally present in foodstuffs; they vary in character from product to product and, even in the same product, may vary in amount under such influences as season of growth, harvesting conditions¹³ and sterilising procedures^{15,16}. The reduction of colouring matters in fruit has already been mentioned; other organic compounds in fruit and vegetables may be reduced and, in fish, trimethylamine oxide is a known large stimulator of corrosion. Inorganic nitrate, which is reduced to ammonia, is a most damaging promoter of corrosion in many vegetables and in fruit at pH values below 5.5¹⁷. If cathodic depolarisers are present in amounts sufficient to promote dissolution of a substantial amount of tin coating then the best means of obtaining satisfactory can appearance and shelf-life is to use lacquered tin-plate. Passivation films are not a reliable means of preventing etching of the tin coating. In the more acid media they are removed wholly and, in some slightly corrosive products such as milk, the films break down locally where the surface has been slightly damaged in can manufacture and unsightly local corrosion then occurs.

Although lacquering is used increasingly for can interiors, there are advantages in cost and in preserving the flavour and colour of some products for the use of plain tinplate. With plain cans, deferment of serious hydrogen evolution can be obtained by increasing the thickness of the tin coating but the preferred method is to control characteristics of the coating and steel base in manufacture, checking achievement by suitable tests. Control measures in use are:

1. To limit the content in the steel of phosphorus, sulphur and 'tramp' elements such as copper, nickel and chromium¹⁸.
2. To avoid the slight oxidation of the steel surface during the bright-annealing process that precedes tinning^{19,20}. The harmful, so called 'pickle-lag layer' so produced is detected by its resistance to 10 N HCl.
4. To limit the total porosity of the coating, checking by the Iron Solution Value (ISV) test in which samples are immersed under standard conditions in a solution of sulphuric acid, hydrogen peroxide and ammonium thiocyanate, and the amount of iron dissolved is measured¹⁹.
5. To ensure maximum continuity of the tin-iron compound layer between tin and steel. This layer is itself corrosion resistant and appears to act as a nearly inert screen limiting the area of steel exposed as tin is removed by corrosion. Its effectiveness is measured by the Alloy-Tin Couple (A.T.C.) test, in which the current flowing is measured between a sample of tinplate from which the unalloyed tin layer has been removed, and a relatively large tin electrode immersed in an anaerobic fruit juice²¹⁻²³.

Tinplate that meets the rigid specifications imposed by these controls is sometimes supplied as special quality material and undoubtedly can give improved shelf-life, particularly with citrus fruits. The A.T.C. value has probably more effect on shelf-life determined by hydrogen swell than any other factor.

A limited degree of control over the corrosivity of the product packed is possible. Minor pH adjustments may be helpful, especially in ensuring an anodic relation of tin to steel; corrosion promoters, like nitrate, sulphur and copper may be excluded from necessary additives, such as water and sugar, and from sprays applied to crops approaching harvest. The effect of sulphur compounds which may remain from spray residues is complex²⁴ but often includes reversal of the tin-iron polarity.

The use of lacquered tinplate does not automatically guarantee freedom from serious corrosion. The covering of the tin surface largely denies both corrosion inhibition by dissolved tin and cathodic protection to any steel exposed at coating discontinuities. Consequently, if discontinuities exist, perforation of cans and hydrogen swells are possible. Lacquer is applied to the tinplate before it is made into cans so that there is a risk, especially at seam areas, of scratching through or cracking of the coating. The dangers are minimised by suitable choice of lacquer and, for critical packs, by double coating and by applying a stripe of lacquer to the seam after can manufacture. The tin coating is not entirely without influence and coating thicknesses may still influence performance^{25,26}. In general, the coating properties found desirable for the plain can are not likely to be so important for the lacquered can, although steel quality remains an important factor.

Requirements for cans for beer and soft drinks differ from those for food cans in that (a) only low tin and iron contents can be tolerated in the product and (b) the anticipated shelf-lives are much shorter. Specialised lacquering techniques including striping the seams are used to give complete cover to the metal. For soft drinks it is sometimes possible to select colouring matters and acids least likely to give rise to corrosion troubles, and rapid methods of testing formulations have been devised²⁷. Steel quality is also controlled by special tests.

Tinned copper and copper alloys Copper itself has a fair corrosion resistance but traces of copper salts are often troublesome and a tin coating offers a convenient means of preventing their formation. Thus copper wire to receive rubber insulation is tinned to preserve the copper from sulphide tarnish and the rubber from copper-catalysed oxidation, and also to keep the wire easily solderable. Vessels to contain water or foodstuffs, including cooking vessels, water-heaters and heat exchangers, may all be tinned to avoid copper contamination accompanied by possible catalysis of the oxidation of such products as milk, and discolouration in the form of, for example, green stains in water and food.

Tin is anodic to copper in water supplies and in all solutions except those in which copper is dissolved as a complex, e.g. strong ammonia solutions. In water supplies the corrosion of the tin coating is, like that of tin, localised, but once the copper is reached it may spread slowly. This simple behaviour can, however, be considerably altered by the action of tin-copper compound layers in the coating. A hot-dipped or wiped coating will have from the outset a layer of Cu_6Sn_5 and perhaps also another, nearer the copper, of Cu_3Sn . Even an electrolytic coating will in time develop a compound layer by diffusion, at a rate depending on temperature; in boiling water the formation of the compound consumes about $2.5 \mu\text{m}$ of the coating per year.

The compounds are always cathodic to tin; in a wiped coating, which usually has streaks of compound in the surface, this has the effect of increasing the extent of local corrosion of tin with the production of unsightly black streaks. In addition, the compound Cu_6Sn_5 can be cathodic to copper; this behaviour is favoured by mild oxidising conditions, which ennoble the compound, and water movement, which anodically depolarises the copper. So long as some tin coating remains it will protect the copper, and a complete coating of compound is protective, but if all the coating is converted to compound and if there is a break in it which exposes copper, then pitting can occur. Adequately thick tin coatings and re-tinning of equipment when necessary are the proper safeguards.

The unfortunate action of the compound layer is observed only rarely, usually in hot water. In cooking vessels (domestic or industrial) the copper is protected satisfactorily at some sacrifice of tin, and occasional re-tinning ensures long service. In atmospheric corrosion the arrival of compounds at the surface of the coating results in some darkening and in loss of solderability.

With tin coatings on brass, the interdiffusion of coating and substrate brings zinc to the surface of the tin: the action can be rapid even with electrodeposited coatings. The effect of zinc in the surface layers is to reduce the resistance of the coating to dulling in humid atmospheres, and the layer of zinc corrosion product formed makes soldering more difficult. An intermediate layer of copper or nickel between brass and tin restrains this interdiffusion²⁸.

Since galvanic action (Section 1.7) between tin and aluminium alloys is slight, tin coatings are often applied to copper and copper alloys which are to be used in contact with these metals. Both direct galvanic action and corrosion resulting from copper dissolving and re-depositing on the light alloy are prevented by this means.

Applications of tin coatings The properties of tin coatings which are advantageous in most of their applications are: fair general resistance to corrosion except in strongly alkaline or acid environments, lack of colour, toxicity or catalytic activity of any corrosion product formed, and ease of soldering. The ready availability of coated steel sheets in the form of tinplate, which has a bright appearance and is easy to form and receptive to decoration and protective finishes, is also an advantage.

The main application is in the form of tinplate. Apart from its use for containers mentioned earlier, tinplate is made into domestic and industrial kitchen equipment, light engineering products and toys. For most of these purposes, coatings in the thickness range 0.4–2.5 μm , with or without organic finishes, are used. For returnable containers and more permanent articles such as fuel tanks and gas-meter cases, heavier coatings of up to 15 μm may be necessary.

Hot-dipped and electrolytic coatings are applied to vessels and equipment made of steel, cast iron, copper or copper alloys for use in the food industry, and to wire and components for the electrical and electronics industries, where ease of soldering is an essential property. Although tin coatings are not immune from damage by fretting corrosion, and fretting between tinplate sheets in transit sometimes produces patterns of black spots, tin coatings may be used to reduce the risk of fretting damage in press fits and splined joints of steel components²⁹. The coating packs the joint and any movement takes place within the coating. An allied application is the tinning of aluminium alloy or iron pistons to provide a suitable working surface during the running-in period³⁰.

Sprayed coatings find a use in large vessels and some equipment used in the food industry. The necessity for these coatings to be thick enough to be pore-free has already been mentioned.

As a general guide to the thickness of coating desirable for various applications, the requirements of BS 1872:1964 for electrodeposited tin coatings are shown in Tables 13.12 and 13.13.

For many purposes involving contact with food and water, coatings

Table 13.12 Thickness suggested for electrodeposited tin coatings on ferrous components

<i>Purpose</i>	<i>Minimum local thickness (μm)</i>
Contact with food or water where a complete cover of tin has to be maintained against corrosion and abrasion	30
Protection in atmosphere	20
Protection in moderate atmospheric conditions with only occasional condensation of moisture	10
To provide solderability and protection in mild atmospheres	5
Coatings flow-brightened by fusion (solderability and protection in mild atmospheres)	2.5 (maximum 8)

Table 13.13 Thickness suggested for electrodeposited tin coatings on copper and copper alloys with at least 50% copper

<i>Purpose</i>	<i>Minimum local thickness (μm)</i>
Contact with food or water where a complete cover of tin has to be maintained against corrosion and abrasion	30
Protection in atmosphere and in less aggressive immersion conditions	15
To provide solderability and protection in mild atmospheric conditions	5*
Coatings flow-brightened by fusion (solderability and protection in mild atmospheres)	2.5* (maximum 8)

* On brass an undercoat of copper, nickel or bronze of thickness 2.5 μm is required.

thinner than those specified in the first category are sometimes sufficient; much depends on the expected amount of abrasion, or loss during cleaning processes. Hot-dipped coatings in the usual thickness range of 10–25 μm give good protection to water-heaters, dairy equipment and much industrial plant, and the thinner coatings of the tinplates in common use are usually sufficient with proper care to preserve appearance in storage and transport. On the other hand, on copper for hot-water service it may sometimes be desirable to use coatings thicker than those recommended in view of the risk in interdiffusion between tin and copper.

Tin Alloy Coatings

Tin-lead

Tin-lead coatings with upwards of 5% lead may be applied by hot dipping to steel, copper and copper alloys. Steel sheets are commonly coated with alloys containing 7%, 10% or 25% tin; these are called *terne-plate*, with the name *tin-terne* sometimes applied to the higher tin-content coating. Tin-lead alloys may also be electrodeposited from a fluoroborate solution containing organic addition agents and bright deposits are possible.

These alloy coatings have advantages over tin in atmospheric exposure where there is heavy pollution by oxides of sulphur. They are cathodic to steel and anodic to copper. In industrial atmospheres, however, formation of a layer of lead sulphate seals pores and produces a generally stable surface³ and *terne-plate* has been used extensively as roofing sheet, especially in the USA. It is easily and effectively painted when additional protection is required. Copper heat exchangers in gas-fired water-heaters may be coated by hot dipping in 20% tin alloy³¹.

Tin-lead alloy coatings have some of the susceptibility of lead to vapours

of organic acids such as acetic acid, and may be attacked by vapours from wood and insulating materials when enclosed in wooden cases or in electrical apparatus. They are, however, widely and successfully used as protective and easily solderable coatings on wire, electronic components and printed circuit boards.

Tin-lead can be substituted for tin for other purposes, although the toxicity of lead limits the field of application. The corrosion resistance is usually no better than that of unalloyed tin, but there may be some saving of cost in applications such as wash-boilers and other vessels for non-potable liquids and light engineering components formed from sheet metal. Heavily coated terne-plates may be used for the fuel tanks of stoves and vehicles.

Tin-zinc

Tin-zinc alloys of a wide range of composition can be electrodeposited from sodium stannate/zinc cyanide baths; only the coatings with 20–25% zinc have commercial importance^{32,33}.

There is no intermetallic compound formation and the electrodeposit behaves as a simple mixture of the two metals. It can be considered as basically a stable wick of tin through which zinc is fed to be consumed at a rate lower than its consumption from a wholly zinc surface. If the conditions are such that zinc is rapidly consumed, and no protective layer of corrosion products is formed, the coating may break down, but in mildly corrosive conditions some of the benefits of a zinc coating, without some of its disadvantages, are obtained.

In condensed moisture, there is sufficient corrosion of zinc to give protection at pores in a coating on steel without the formation of as much zinc corrosion product as would develop on a wholly zinc surface. In solderability the coating is tin-like when new or stored dry, but the selective corrosion of zinc in humid conditions may produce a layer obstructive to easy soldering.

In full weathering in industrial areas, the zinc is taken from the coating too quickly and the alloy coatings do not endure as long as either zinc or tin coatings of comparable thickness; they may, however, outlast cadmium³⁴. By the sea, the alloy coatings are somewhat better, and in more continuously wet conditions, such as at half-tide positions, they may outlast zinc coatings; possibly here the corrosion product is protective. It is, however, in sheltered conditions and special environments that tin-zinc is most useful. Its easy solderability combined with protection at pores makes it applicable in electrical and radio equipment and in components of tools and mechanisms. It is also used on the bodies of water-containing fire extinguishers, and on components exposed to hydraulic fluids.

The coating is, in addition, useful in preventing galvanic corrosion³⁵. Plated on steel which is to be used in contact with aluminium alloys, it protects the steel and does not stimulate the corrosion of the light alloy and is itself not consumed as rapidly as a 100% zinc coating.

Tin-cadmium

Tin-cadmium alloys of a range of compositions can be deposited from stannate/cyanide solutions or fluoride/fluorosilicate solutions³⁶. The behaviour of the coatings is rather similar to that of tin-zinc, but as cadmium is less effective than zinc in giving cathodic protection to steel, a 25% cadmium coating is barely able to protect pores and a 50% content is better for this purpose. The coatings in some conditions form an extremely dense layer of corrosion product, and give an outstanding performance in laboratory salt-spray tests³⁷, but there has been no substantial practical application. Coatings of tin over cadmium, which combine an inert outer surface with protection from rusting at pores, have been used on containers of solvents and to protect electrical components against organic vapour corrosion.

Tin-copper

Tin-copper alloys may be electrodeposited from copper cyanide/sodium stannate baths³⁸ or from cyanide/pyrophosphate baths³⁹ to give a range of compositions. Alloys with 10–20% tin have a pleasant golden colour but are not tarnish-resistant unless coated with lacquer. The alloy with 42% tin known as *speculum* is silver-like in colour and is resistant to some forms of corrosion. At this composition the deposit is formed as the intermetallic compound Cu_3Sn . It has a useful hardness (about 520 H_V). The deposit becomes dull on exposure to atmospheres containing appreciable amounts of sulphur dioxide, but resists hydrogen sulphide, and remains bright in the more usual indoor atmospheres. Although out of doors it becomes dull and grey if not cleaned frequently, the coating is very suitable for metalwork used indoors; it resists the action of most foodstuffs and is suitable for tableware. Like many intermetallic compounds, the deposit shows a corroding potential which becomes increasingly noble with duration of immersion in electrolyte. It is strongly cathodic to steel, and pore-free deposits are desirable. Recommended minimum thicknesses are 12 μm on brass, copper, nickel silver, etc. and 25 μm on steel.

The fact that the composition of the speculum deposit must be closely controlled to obtain the best results has been a serious drawback to development. The coating finds uses on decorative hollow-ware, oil lamps and tableware. The bronze deposits with 10 or 20% tin are used lacquered in decorative metal-ware for domestic and personal ornament and, in thick layers to protect hydraulic pit props against corrosion and abrasion. They have also been used with success as undercoatings for nickel-chromium^{39,40} or tin-nickel alloy deposits.

Tin-nickel

Tin-nickel alloy coatings are deposited from a bath containing stannous chloride, nickel chloride, ammonium bifluoride and ammonia^{41,42}. The useful deposit contains 65% tin and the conditions are maintained to obtain

this composition only; control is, fortunately, easy. A special feature of the process is the good throw of deposit into recesses.

The deposit plates out as the intermetallic compound NiSn, which is white with a faintly pink tinge, and has a hardness of about 710 H_v. Deposits from new baths are usually in tensile stress but those from baths used for some time are in compressive stress; the stress can be controlled if desired by adjustment of solution composition⁴³. The properties of the intermetallic compound differ from those of both the constituent metals. It is easily passivated, resisting concentrated nitric acid and becoming considerably ennobled during immersion in solutions of neutral salts, including sea-water. In a wide range of solutions, the potential of NiSn with reference to the standard hydrogen electrode was, on immediate immersion, +0.33–0.055 pH and, after some hours, +0.59–0.056 pH⁴⁴. Higher potentials are reached after long immersion or in oxidising conditions, but ennoblement occurs in solutions with extremely low oxygen concentrations; evidence for five oxidation states for the surface film has been obtained, one at the low potential of –0.42–0.06 pH⁴⁵. The film thickening that accompanies this change to a more noble potential may become visible, and in hot water or steam a purple film may be produced.

The deposit resists atmospheric tarnish even in the presence of high pollution by sulphur dioxide (in contrast to nickel) and hydrogen sulphide, and coatings exposed to the outdoor atmosphere remain bright indefinitely, sometimes taking on a slightly more pink colour as the oxide film thickens.

The passivity at pH values above about 1.5 is maintained in a great variety of solutions, including fruit juices, vinegar, sea-water, alkalis, and even ferric chloride⁴⁶. Hot caustic alkali solutions above about 10% attack the coating slowly, and the halogens etch it.

The nobility of the coating brings with it the handicap that corrosion of base metal exposed at pores is stimulated. In an electrolyte of good conductivity, steel, brass or copper are attacked freely at pore sites; steel plates 1 mm thick were perforated after 12 months in the sea. In the outdoor atmosphere, the rate of penetration of the basis metal is slow, but disfigurement by the appearance of corrosion products at pore sites may occur^{46,47}. Since the coating itself is not attacked, new pores do not develop during atmospheric exposure, so that the risks of corrosion at pores can be mitigated by attention to the original condition of the coating. Deposits more than 30 μm thick will usually be pore-free, and for deposits on steel for outdoor exposure an undercoating of copper is decidedly advantageous^{47,48}. The copper undercoat, preferably about 12 μm thick, reduces the number of pores penetrating from the surface to the steel, and in industrial atmospheres tends to reduce corrosion at such pores as remain. Tin or tin-copper alloy undercoats may also be used and in marine environments are somewhat better than copper.

Indoors, pore corrosion is troublesome only if there are prolonged periods of wetting by condensed moisture, and coating thicknesses may safely be much less than those desirable out of doors. The coating will not, however, withstand much deformation, and even with the thinner coatings plating should, if possible, be carried out after all forming operations are complete.

The application of the tin-nickel coating for out of doors service has been restricted by fear of pore corrosion and of physical damage, and by

the poor colour match with chromium. For indoor use, the coating has many applications, e.g. laboratory instruments, balance weights, the valves of wind instruments, internal mechanism of watches, electrical instruments, lighting fittings, interiors of cooking vessels and decorative hollow-ware. Many of these are special applications in which, in addition to corrosion resistance, the hard, smooth surface, non-magnetic quality and the good covering power in deposition of the coatings, may have been required.

These qualities have also lead to its use on printed circuit boards and on electrical connectors, although the persistent oxide film obstructs easy solderability and produces too high a contact resistance for satisfactory switching at low voltages.

Recent Developments

Tin Coatings

Recent work^{50,52} has shown that tin may be deposited by an autocatalytic process using transition-metal ion reducing agents. Very thick coatings may also be economically applied to a variety of substrates by the process of roll bonding⁵³.

Tinplate still represents the largest use for tin, but continuing developments in can-making technology mean that coatings as thin as $0.1 \mu\text{m}$ are in use⁵⁴. These may be non-reflowed, reflowed to produce a duplex tin and tin-iron alloy coating, or reflowed to convert all of the tin coating to tin-iron alloy. These products are almost exclusively used in the lacquered condition but the presence of tin still plays a significant role in controlling the corrosion of the steel basis material. In some cases, the properties of the coatings are modified significantly by the application of a passivation film consisting of a mixture of chromium metal and chromium oxides and much heavier than that used on tinplate with thicker tin coatings.

The shelf-life of containers made from unlacquered tinplate is now dictated by national and international regulations governing the permitted tin content of foods. Since the onset of hydrogen swells is usually during the later stages of plate detinning during service, the value of the A.T.C. test in predicting container shelf-life is severely limited.

General thickness requirements for electroplated tin coatings on ferrous and non-ferrous substrates are contained in BS 1872:1984 and ISO 2093 and these are essentially the same as those in Tables 13.12 and 13.13.

Tin Alloy Coatings

The corrosion resistance of tin-lead alloy coatings on copper and copper alloys is directly relevant to their use in the electronics industry. The solderability of coatings as a function of storage time has been reported⁵⁵ and accelerated ageing techniques have been compared⁵⁶. The electrical contact resistance of tin-lead coatings increases in some atmospheres⁵⁷⁻⁵⁹, although the film of corrosion products is easily ruptured when contacts are mated⁶⁰. General requirements for tin-lead coatings are contained in BS 6137:1982.

There has been some renewed interest in the use of tin-zinc alloy electroplate as a substitute for cadmium coatings on steel^{61,62}. It has been pointed out that tin-zinc coatings produce less loose corrosion product than zinc during full outdoor exposure⁶³.

In view of the difficulties in controlling the electroplating of speculum and bronze coatings, alternative preparation routes through the heat treatment of duplex tin and copper electroplated finishes have been proposed⁶⁴.

The resistance of tin-nickel alloy electroplate to corrosion has been the subject of recent studies using surface analytical techniques. Workers generally agree that the surface of NiSn electroplate exposed to the atmosphere is enriched with tin oxide⁶⁵⁻⁶⁹, and that this probably also applies to other nickel-tin intermetallic compounds⁷⁰. The interaction of coatings of NiSn, Ni₃Sn₄ and Ni₃Sn₂ with SO₂, H₂S, NH₃, NO₂, sulphur vapour, salt-spray and synthetic dust have been monitored with particular reference to electrical resistance⁷¹. Changes seen have been related to the structure of the passivation film⁷², and the advantages in using tin-nickel alloy electroplate as an undercoat for the very thin gold deposits used in electrical contacts have been described⁷³. The requirements for tin-nickel alloy electroplate are contained in BS 3597:1984.

Electroplated coatings based on deposits containing tin and cobalt are now available as substitutes for chromium plating. Deposits corresponding to CoSn^{74,75} or CoSn mixed with CoSn₂⁷⁶ may be obtained which show a good colour match with chromium and a number of proprietary processes have been patented. Most studies of the corrosion of tin-cobalt alloy deposits have been concerned with the performance of thin coatings (0.5 µm) over nickel. It has been noted⁷⁷ that the coating performs well in salt-spray and CASS tests and that it resists ammonia: comparisons have been made with a nickel-chromium finish and it was found that tin-cobalt alloy on nickel deposits perform as well as the conventional coating in all but the most severe exposure conditions^{78,79}. While the ductility of tin-cobalt coatings is greater than that for tin-nickel deposits⁷⁷, the corrosion resistance of each finish is very similar⁸⁰. As with tin-nickel, it has been shown that tin-cobalt deposits have surface enrichment by tin oxides⁸¹.

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13.6 Copper and Copper Alloy Coatings

Copper coatings are usually applied by electrodeposition (Section 12.1), although for more limited purposes 'electroless' or immersion deposits are used. Less frequently, copper may also be applied by flame spraying¹.

Applications

Copper deposits are applied predominantly for the following purposes:

1. As an undercoat for other metal coatings. The main use of copper plating is as an undercoating prior to nickel-chromium plating steel and zinc-base die castings. On steel, the primary purpose is to reduce polishing costs. Other advantages are that with a copper-plated undercoating, cleaning is less critical for achieving a well-adherent nickel deposit and metal distribution is frequently improved. Nickel-chromium plating standards of most countries permit some part of the nickel thickness to be replaced by copper^{2,3}. On zinc-base die castings a copper undercoat is almost universally used, as an adherent nickel deposit cannot be deposited directly from conventional baths. For a similar reason copper is deposited on aluminium which has been given an immersion zinc deposit⁴ before nickel plating is applied.

Under micro-discontinuous chromium coatings, copper undercoats improve corrosion resistance. On non-conductors, especially on plastic substrates, copper is often applied before nickel-chromium plating over the initial 'electroless' copper or nickel deposit in order to improve ductility and adhesion, e.g. as tested by the standard thermal-cycling test methods⁵.

2. As a decorative finish on steel and zinc-base alloys for a variety of domestic and ornamental articles. The finish may be protected by clear lacquers or may be coloured by metal colouring techniques for use on, for example, door handles, luggage trim, etc.

3. As a 'stop-off' for nitriding or carburising of steel. The 10–40 μm deposits, which are electroplated on selected areas, are removed after the heat treatment.

4. For protection of engineering parts against fretting corrosion, on electrical cables and on printing cylinders. Temporary protection allied with lubrication is provided by immersion deposits of copper on steel wire.

5. Chemical deposits of copper are applied to provide conducting surfaces on non-metallic materials.

6. Copper is plated on printed circuit boards to provide electrical conductors and for a variety of other electrical and electronic applications⁶.

Plating Solutions

Copper is electrodeposited commercially mainly from cyanide, sulphate and pyrophosphate baths. For rapid deposition in electro-forming, a fluoborate bath may also be used.

The sulphate bath The sulphate bath, the earliest of electroplating solutions and the simplest in composition, contains typically 150–250 g/l of copper sulphate and 40–120 g/l of sulphuric acid. The composition is not critical and the higher concentrations are used for plating at higher current densities, normally up to 6 A/dm².

Addition agents used to produce smooth and fine-grained (though dull) deposits include gelatin, glue, phenol sulphonic acid, hydroxylamine and triethanolamine. These are believed to inhibit crystal growth by forming colloids in the cathode layer, and, in some cases, to change the crystallographic orientation.

Modern bright acid copper plating baths contain both organic and inorganic addition agents which act as brighteners and levellers. The two functions are largely distinct, the latter being the more important when copper is plated as an undercoat for decorative nickel-chromium coatings. Additives of this type include organic sulphur compounds, e.g. thiourea derivatives. Such solutions are sensitive to the chloride ion concentration which must be maintained at a low level.

On ferrous metals immersion deposition in the copper sulphate bath produces non-adherent deposits, and a cyanide copper undercoat is therefore normally used. Where the use of a cyanide strike cannot be tolerated, an electroplated or immersion nickel deposit has been used^{7,8}. Additions of surface-active agents, often preceded by a sulphuric acid pickle containing the same compound, form the basis of recent methods for plating from a copper sulphate bath directly on to steel^{9–11}.

While the sulphate bath has a high plating speed, its throwing power is poor, and this limits its application to articles of simple shapes.

Cyanide baths Most general copper plating, other than that applied, for example, to wire and strip or for electroforming, is carried out in a cyanide bath. Its main advantages are (a) that it can be used to plate directly onto steel and zinc-base alloys, and (b) that it has good throwing power, which renders it suitable for plating a large variety of shapes.

Modern solutions fall mainly into three types: (a) the plain cyanide bath which contains typically 20–25 g/l of copper cyanide, 25–30 g/l total sodium cyanide (6.2 g/l 'free' sodium cyanide), and is operated at 21–38°C and 110–160 A/m²; (b) the 'Rochelle' copper bath to which is added 35–50 g/l of Rochelle salt and which is used at 66°C at up to 645 A/m²; and (c) the high-efficiency cyanide baths which may contain up to 125 g/l of copper cyanide, 6–11 g/l of 'free' sodium or potassium cyanide, 15–30 g/l of sodium or potassium hydroxide, and are operated at up to 6–9 A/dm² and 65–90°C. Most bright cyanide copper baths¹² are of the high-efficiency type and, in addition, contain one or more of the many patented brightening and levelling agents available. Periodic reverse (p.r.) current is also sometimes used to produce smoother deposits.

Plating speeds for the high-efficiency baths are high, partly because higher current densities can be used without 'burning', but mainly because the

cathode efficiency of the more concentrated solution is higher at higher current densities (e.g. 90–98% compared to 30–60% for the 'plain' and 'Rochelle' type solutions). However, a more dilute solution must generally be used as a 'strike' bath on steel and zinc-base alloys to avoid immersion deposition.

Pyrophosphate bath The pyrophosphate bath is intermediate in throwing power between the sulphate and cyanide baths. A typical bath contains 80–105 g/l of copper pyrophosphate, 310–375 g/l of potassium pyrophosphate and 25 g/l of potassium citrate, pH 8·7–9·4. Similar baths containing nitrate, ammonia and oxalate are also employed. The solutions are used at 50–60°C with vigorous air agitation when current densities of up to 10 A/dm² are permissible. A proprietary bath is available with excellent brightening and good levelling characteristics.

A more dilute strike bath is employed for obtaining the initial deposit on steel, while for strongly recessed parts, e.g. tubular work, an immersion nickel deposit has been used⁸. A short cyanide copper strike is used before plating on zinc-base die castings.

Other electroplating solutions Other solutions¹², which are more rarely used for plating copper, include the fluoborate bath, the amine bath, the sulphamate bath and the alkane sulphonate bath.

Chemical deposition Simple immersion deposits of copper may be obtained on iron and steel in a solution containing, for example, 15 g/l of copper sulphate and 8 g/l sulphuric acid, and on zinc-base alloy in a solution containing copper sulphate 300 g/l, tartaric acid 50 g/l and ammonium hydroxide 30 ml/l¹³. Such deposits are thin and porous and are mainly plated for their colour, e.g. for identification, or for their lubricating properties, e.g. in wire drawing.

Solutions containing tetrasodium E.D.T.A. have also been used for this purpose and give slightly superior coatings.

On non-conductors, copper may be deposited by chemical reduction from a modified Fehling's solution. Such solutions have gained wide application in the plating of ABS and other plastics which are 'electrolessly' copper plated before nickel-chromium plating. Pretreatment of the plastic is important in order to gain adequate adhesion and includes steps for etching the surface as well as for providing a conducting substrate by treatment in stannous chloride and palladium chloride solutions.

Properties of Copper Deposits

Deposit uniformity The uniformity of a deposit is an important factor in its overall corrosion resistance and is a function of geometrical factors and the 'throwing power' of the plating solution. A distinction is made here between macro-throwing power, which refers to distribution over relatively large-scale profiles, and micro-throwing power, which relates to smaller irregularities¹⁴.

The copper cyanide bath has excellent macro-throwing power and is chosen whenever irregular-shaped parts are to be plated. The sulphate bath is not inferior when parts with very narrow recesses, i.e. with width of opening less than 6 mm, are to be plated, although its macro-throwing power is

poor. Pyrophosphate baths are intermediate between the two in macro-throwing power.

Porosity As is the case with all cathodic deposits, the corrosion resistance of a copper deposit is reduced in the presence of continuous porosity. Experience has shown that porosity is least when attention is paid to adequate cleaning, and the solution is kept free from solid or dissolved impurities (see Section 12.1). Porosity of copper deposits is also related to polarisation¹⁵.

Corrosion resistance The corrosion resistance of a copper deposit varies with the conditions under which it is deposited and may be influenced by co-deposited addition agents (see, for example, Raub¹⁶). Copper is, however, plated as a protective coating only in specialised applications, and the chief interest lies in its behaviour as an undercoating for nickel-chromium on steel and on zinc-base alloy. Its value for this purpose has long been a controversial issue.

A thin copper deposit, e.g. 2.5 μm , plated between steel and nickel, improves corrosion resistance during outdoor exposure¹⁷, and many platers also believe that a copper undercoating improves the covering power of nickel, particularly on rough steel.

Where heavier copper coatings are plated as a partial replacement for nickel, as is permitted under most nickel plating specifications, the effects are not clearly established. According to Blum and Hogaboom¹⁸ the protective value of nickel on steel is reduced by the presence of a copper undercoating, but this does not apply when the nickel is chromium plated. This is largely corroborated by subsequent corrosion tests^{17,19} and the detrimental effect in the absence of chromium is probably due to attack on the nickel by the copper corrosion products. In the presence of conventional chromium plate, on the other hand, the fact that statistical evidence on many thousands of chromium-plated motor components has not established any difference in the behaviour of parts in which nickel formed respectively 95–100% and 50% of the copper-nickel coating²⁰, bears out the view that after chromium plating the differences in protective value tend to disappear. Moreover, when, as frequently happens in practice, the copper coating is polished, the protective value of the copper-nickel coating is higher than that of nickel alone, owing to the pore-sealing effect of the polishing operation.

The case is different again under micro-discontinuous (i.e. micro-cracked or micro-porous) chromium, on which a definite improvement in corrosion resistance can be achieved when copper is present under the nickel coating^{21,22}.

As an undercoating for chromium, i.e. in place of nickel, copper is not to be recommended. On the other hand, both accelerated and outdoor corrosion tests have shown that a tin-bronze deposit, containing 80–90% copper, is considerably better for this purpose and it has been claimed to be approximately equal to nickel in this respect.

Mechanical properties The hardness and strength of copper deposits may vary widely according to the type of bath used (see Table 13.14). In the presence of addition agents which decompose in use, the hardness may, moreover, vary appreciably with the age of the bath²³.

In copper sulphate solutions, hardness and tensile strength are increased

Table 13.14 Mechanical properties of electrodeposited copper¹²

Plating bath	Hardness (HV)	Elongation [% on 50.8 mm (2 in)]	Tensile strength (MN/m ²)
Sulphate bath	40-65	20-40	230-310
Sulphate bath with addition agent	80-180	1-20	480-620
Fluoborate bath	40-75	7-20	240-275
Cyanide bath	100-160	9-15	415-550
Cyanide bath with p.r. current	150-220	6-9	690-760
Pyrophosphate bath	125-165	—	—

by raising the current density and reducing the temperature. As will be seen from Table 13.14, particularly high hardness values can be obtained in the cyanide bath by using p.r. current.

Annealing of electrodeposited copper reduces the mechanical properties. As an example, the tensile strength has been reported to decrease from 275-330 MN/m² to 180-255 MN/m² on heating at above 300°C²⁴ while the hardness of deposits obtained in the presence of addition agents may drop from as high a value as 300 HV to 80 HV after annealing at 200°C.

Internal stress of copper deposits may vary between -3.4 MN/m² (compressive) and +100 MN/m² (tensile). In general, tensile stress is considerably lower in deposits from the sulphate bath than in those from cyanide solutions²⁵⁻²⁷, while pyrophosphate copper deposits give intermediate values. In cyanide solutions, tensile stress increases with metal concentration and temperature decreases if the free cyanide concentration is raised. P.r. current significantly lowers tensile stress²⁸. With some exceptions, inorganic impurities tend to increase tensile stress²⁹. Thiocyanate may produce compressive stress in cyanide baths²⁵.

In the sulphate bath the tensile stress increases if the temperature is reduced or the current density is increased, and gradually diminishes with increase in deposit thickness²⁵. Addition of thiourea (1 g/l) or gelatin to the acid bath results in compressively stressed deposits, though at higher concentrations of addition agent this effect may be reversed³⁰. Dextrose and gum arabic increase tensile stress³¹. The effect of other organic compounds may similarly depend on the operating conditions^{32,33}. The relationship between ductility and stress is complex, e.g. thiourea additions increase ductility over a wide range³⁴.

Despite the large differences in respect of other mechanical properties, it has been established³⁵ that the wear resistance of copper deposits, which is markedly inferior to, for example, that of electrodeposited nickel, is not significantly affected by either type of bath or addition agents.

Embrittlement by hydrogen absorbed by the substrate during pretreatment, e.g. in acid pickling baths or during plating, is generally important only on copper-plated wire or where copper is plated for lubrication before drawing operations on high-strength steels. For these purposes the acid copper bath is slightly preferable to the cyanide bath. Hydrogen may be removed and ductility restored by heat treatment in air (140-200°C for 0.5-1 h), in water (80-100°C for 0.5-2 h), or in oil (175-230°C for 1.5-2 h)¹². Other properties have been comprehensively summarised in the literature^{12,36}.

Copper Alloy Deposits

Copper-zinc Copper-zinc alloys are deposited for two main purposes: (a) as a decorative finish, e.g. on steel and (b) as a means of obtaining an adhesive bond of rubber to other metals.

Cyanide solutions are used almost exclusively. One typical solution contains copper cyanide 26 g/l, zinc cyanide 11 g/l, sodium cyanide (total) 45 g/l and sodium cyanide ('free') 7 g/l¹². This bath is operated at pH 10.3–11.0, 110 A/m² and 27–35°C, with 75 Cu–25 Zn alloy anodes. Many other solutions are used¹², including a special rubber-bonding bath³⁷ and a high-speed bath which is capable of being used at up to 16 A/dm²(^{2, 38}).

Brass deposits normally contain 70–80% copper and 30–20% zinc; the colour does not normally match solid brass of the same composition and may, moreover, vary with the operating conditions and solution composition.

White brass deposits containing 85% zinc and 15% copper have also been plated to a limited extent³⁹, mainly as an undercoating for chromium during the nickel shortage, but they did not prove fully satisfactory.

While brass deposits have a somewhat higher protective value on steel than the equivalent thickness of copper, the deposits tend to tarnish, and when used for decorative purposes bright deposits are normally protected by a clear lacquer.

Copper-tin Although a wide range of copper-zinc alloy deposits can be plated⁴⁰, most experience has been gained with two compositions, i.e. the red copper-rich tin-bronze which contains 90–93% copper and 10–7% tin and the white speculum which contains 50–60% copper and 50–40% tin.

While tin-bronze has been successfully plated as an undercoating for chromium during the nickel shortage^{41, 42} its main use now is as a decorative finish in its own right, because of its pleasing red-gold colour. As in the case of brass, however, the deposits must be protected against tarnishing by a clear lacquer.

Speculum deposits are similar in appearance to silver, but are harder and have good tarnish resistance. Alloys containing only 2% copper and 98% tin are plated on bearing surfaces.

Copper-tin deposits can be plated from cyanide or pyrophosphate^{43, 44} baths and deposits are of good corrosion resistance (approximately equivalent to the same thickness of nickel). Hardness values of up to 314 H_v are obtainable for the copper-rich alloys⁴⁵, and up to 530 H_v for the tin-rich alloys can be obtained. (See also Section 13.5.)

Other alloys Other copper alloys can be plated, including copper-tin-zinc (Alballoy)⁴⁶, copper-nickel⁴⁷, copper-cadmium^{48, 49}, copper-gold and copper-lead⁵⁰.

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13.7 Nickel Coatings

Nickel coatings have long been applied to substrates of steel, zinc and other metals in order to provide a surface that is resistant to corrosion, erosion and abrasion. Most of the nickel is used as decorative coatings 5–40 μm thick, usually under a top coat of chromium about 0.5 μm thick so as to give a non-tarnishing finish. Such coatings are applied to metal parts on cars, cycles, perambulators and a wide range of consumer items; they have also been applied increasingly to plastic components during recent years in order to give an attractive metallic appearance^{1,2}. Decorative nickel coatings are also applied without chromium top coats to products such as spanners, screw-driver blades, keys and can-openers.

About 3% of all nickel used in the form of coatings is employed in engineering applications where brightness is rarely needed and the deposits are relatively thick; these coatings are used for new parts and for reclamation.

Most nickel electroplating is carried out in solutions based on the mixture of nickel sulphate, nickel chloride and boric acid proposed by O. P. Watts³. Typical composition and operating conditions are:

Composition

Nickel sulphate ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$): 240–300 g/l

Nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$): 40–60 g/l

Boric acid (H_3BO_3): 25–40 g/l

Operating conditions

Temperature: 25–50°C

Air agitation

pH: 4.0–5.0

Cathodic current density: 3–7 A/dm²

Mean deposition rate: 40–90 $\mu\text{m/h}$

The Watts solution is a relatively cheap, simple solution which is easy to control and keep pure. The nickel sulphate acts as the main source of nickel ions, though nickel chloride is an additional source. Higher deposition rates can be used when the ratio of nickel chloride to nickel sulphate is raised and some proprietary bright nickel solutions are available in a 'high-speed' version which contains an increased concentration of nickel chloride.

Chloride ions are also needed to ensure satisfactory dissolution of some nickel anodes at usual values of pH and solution temperature. Where sulphur is deliberately incorporated in the anode during manufacture however,

anodic dissolution of the nickel is activated and the chloride in the solution may be reduced or entirely eliminated, depending upon the degree of anodic activation achieved and the maximum anodic current density required. Nickel anodes are usually either (a) bars or sheets fabricated by casting, rolling or extrusion, or (b) strips of electrolytic nickel, pieces of electrolytic-nickel or carbonyl-nickel pellets contained in a basket of titanium mesh. The anodes are held in bags of cotton twill, polypropylene or Terylene in order to prevent metallic particles from entering the solution and causing deposit roughness. Accounts of the anodic dissolution of nickel are given by Raub and Disam⁴, and Sellers and Carlin⁵. (See also Section 12.1.)

At normal current densities, about 96–98% of the cathodic current in a Watts solution is consumed in depositing nickel; the remainder gives rise to discharge of hydrogen ions. The boric acid in the solution buffers the loss of acidity arising in this way, and improves the appearance and quality of the deposit. Although phosphates, acetates, citrates and tartrates have been used, boric acid is the usual buffer for nickel solutions.

A detailed discussion of the function of the constituents of the Watts bath is given by Saubestre⁶. In addition to inorganic constituents, organic wetting agents are often added to prevent pitting of the deposit that might otherwise arise from adhesion to the cathode of small bubbles of air⁷ or hydrogen evolved cathodically. Elimination of pitting and other defects is discussed by Bouckley and Watson⁸.

Decorative Plating

The majority of decorative nickel plating is carried out in solutions containing addition agents which modify growth of the nickel deposit so that a fully bright finish is obtained that is suitable for immediate chromium plating without mechanical finishing. At one time, wide use was made of deposits with brightness achieved through additions of cobalt salts plus formates and formaldehyde^{9,10}, but the use of a mixture of organic addition agents enables deposits to be obtained which are smoother, more lustrous, give bright deposits over a wider range of current densities, and have lower internal stress. In consequence, the bulk of bright nickel plating is carried out in organic bright nickel solutions.

Organic bright nickel solutions Several organic substances are used at appropriate concentrations in these solutions in order to give brightness, levelling and control of deposit stress. Portions of the addition agent molecules are incorporated in the deposit, resulting in a hard, fine-grained coating which has a finely striated structure when etched in section and which usually contains incorporated sulphur. The sulphur causes the deposit to be electrochemically less noble than pure nickel deposits. Decomposition products of the additives form in the solution with use, and at one time they accumulated and impaired the mechanical properties of the plate, eventually necessitating batch purification. In modern solutions however, continuous carbon filtration can be used to remove deleterious organic substances without significant removal of the addition agents themselves.

Brighteners Modern solutions contain a brightener system comprising

several additives which together enable bright deposits to be obtained over a wide range of current densities such as that occurring over a component having a complicated shape with deeply recessed areas. Brighteners are broadly divided into primary brighteners and secondary brighteners, but the division is not sharp.

Primary brighteners have a powerful effect on the deposit and are normally used at low concentrations which are carefully controlled. Metals such as cadmium and zinc act as primary brighteners, as do organic substances such as amino polyarylmethanes, quinoline and pyridine derivatives, and sulphonated aryl aldehydes. Primary brighteners often, especially at higher concentrations, affect adversely the mechanical properties of the deposit.

Secondary or carrier brighteners have a milder effect on the deposit when used alone, and modify the effect of primary brighteners. Judicious combination of primary and secondary brighteners gives fully bright but relatively ductile deposits having low internal stress. Aryl sulphonic acids and sulphonates, sulphonamides and sulphimides frequently act as secondary brighteners.

Combinations of brighteners often behave synergistically, so that the final brightening effect is greater than might have been expected from the individual effects.

Stress reducers Many organic substances used as secondary brighteners also reduce the tendency for the internal stress in the deposit to become tensile. In the absence of primary brighteners, they are able to give zero or even compressive stress in nickel deposits, and thereby find wide application in electroforming where accurate control of deposit stress is vital. Saccharin, *p*-toluene sulphonamide, and mono-, di- and tri-sulphonates of benzene and naphthalene are common stress-reducing agents. Stress is usually measured in nickel deposits by observing the bending induced by plating one side only of a metal strip. Convenient and sensitive developments of this technique are available¹¹⁻¹⁴.

Levelling agents A nickel plating solution is said to have levelling action if deposits from it, when applied to an uneven cathode surface, become increasingly smooth as plating proceeds. Levelling agents are therefore widely used to eliminate expensive final polishing of the nickel surface and to reduce the fineness of the surface finish needed on the substrate surface. Both features reduce the cost of producing a bright and smooth finish on a plated article.

Levelling agents increase cathode polarisation and are consumed at the cathode by decomposition or incorporation in the deposit. They are used at a concentration sufficiently low that a diffusion layer is established at the cathode surface, and then the levelling agent is able to diffuse at a greater rate to peaks than to recesses on the surface. In order that the layer of solution adjacent to the cathode surface shall remain an equipotential surface, the current density at recesses rises above that at peaks, giving progressive smoothing of the deposit as deposition proceeds.

The levelling action of an addition agent¹⁵ depends upon its concentration *C* in the solution, the rate of change of cathode potential with change of concentration (dE/dC) and the rate of change of cathode potential with current density (dE/dI). Levelling power (L.P.) at a given current density, defined

as deposit thickness in recesses minus thickness at peaks divided by average thickness, may be expressed as

$$\text{L.P.} = KC(dE/dC)(dI/dE)$$

where K is a constant. Typical levelling agents include coumarin, quinoline ethiodide, butyne 1,4 diol and its derivatives, and thiourea and its derivatives at certain concentrations. Extensive studies of the mechanism of levelling have been carried out in the United States¹⁶, Britain¹⁵ and the Soviet Union¹⁷.

Semi-bright solutions Maximum levelling action is often found in solutions which do not give a fully bright deposit, but the deposit is smooth and can easily be lightly buffed to give a lustrous finish; moreover, many levelling agents used are sulphur-free, so that the deposits are also free from sulphur and as noble as a Watts deposit when subjected to corrosive attack. This feature is exploited in double-layer nickel coatings (see below).

Wetting agents As mentioned earlier, wetting agents are added to nickel solutions to prevent pitting. These wetting agents can be cationic, non-ionic or anionic in nature. In general, the best anti-pit agents tend to produce the most foaming, and a compromise must be struck. Where mechanical agitation of the solution is used, by stirrers or by cathode movement, a greater tendency to foaming can be tolerated than when air-agitation is employed.

Interaction of addition agents The success of modern proprietary bright nickel solutions has resulted in large measure from the skill of the research departments of plating supply houses in balancing the effects of various additives to give optimum results. The detailed findings are usually kept confidential, but the broad principles of addition agent action and interaction are discussed in published work¹⁸⁻²⁰.

A commercial-scale operation with bright and semi-bright solutions based not on Watts but on a solution having nickel sulphamate as the main constituent (430–450 g/l), is described by Siegrist²¹.

Decorative Coating Systems that give Improved Resistance to Corrosion

Double-layer nickel coatings These coatings have an undercoat of highly-levelled sulphur-free nickel covered with sufficient bright nickel to give a fully bright finish with minimum requirement for expensive mechanical finishing of the part. They were initially produced simply to reduce costs, but it was soon noticed that, because the undercoat of sulphur-free semi-bright nickel is electrochemically more noble than the final bright nickel above it, corrosive attack when it does occur is preferentially directed towards the bright nickel, and penetration to the basis metal is markedly delayed.

Figure 13.7 shows how pits in a single-layer nickel deposit start at small pores or other imperfections in the chromium top coat²². The pits are initially hemispherical; those shown here were produced by 6 months in an industrial atmosphere on a copper plus nickel plus chromium plated car bumper.

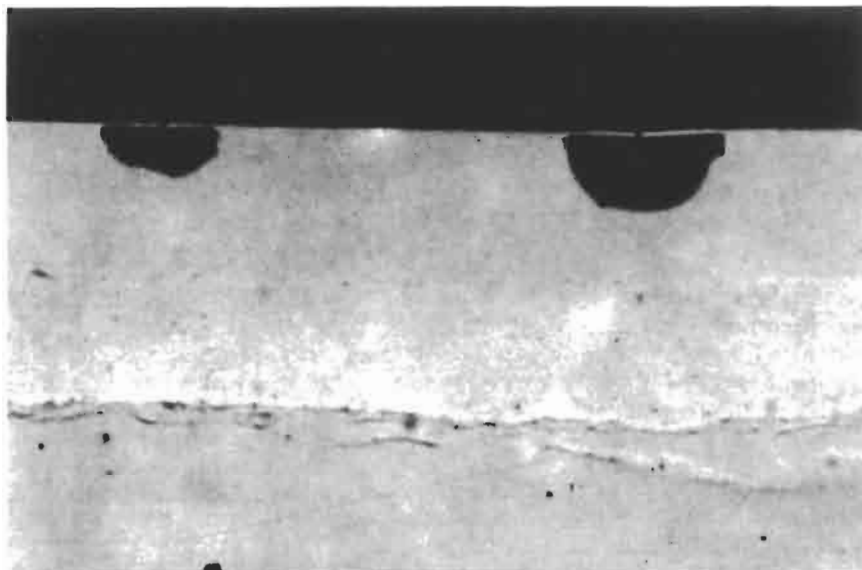


Fig. 13.7 Commencement of corrosion at discontinuities in chromium topcoat over nickel;
× 1 000 (after Reference 22)

In double-layer nickel coatings however, a flat-based pit is formed in the nickel coating, giving marked resistance to penetration to the basis metal. Figure 13.8 shows a pit in a double-layer nickel plus chromium coating after 58 months service.

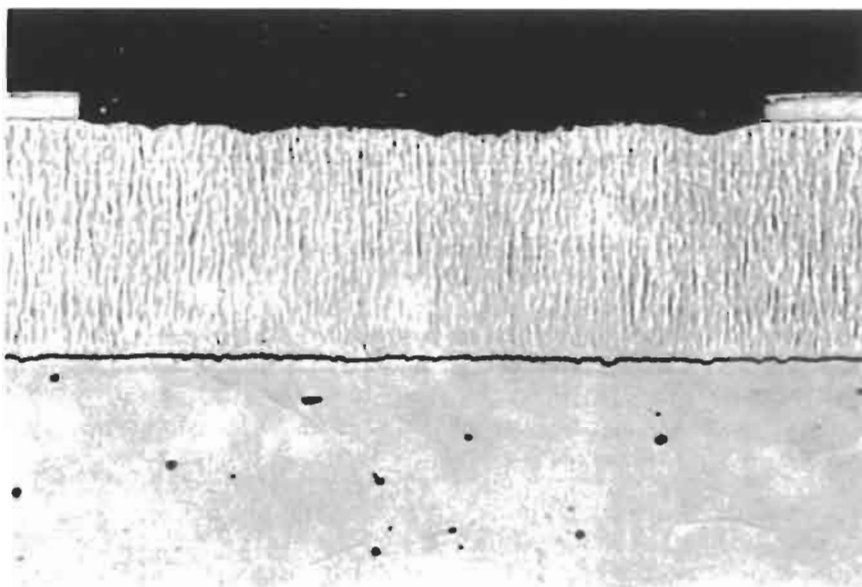


Fig. 13.8 Flat-based pit in double-layer nickel plus chromium coating after 58 months service;
× 300 (after Reference 22)

Triple-layer nickel coatings In order to minimise the effect of corrosive attack on the appearance of the deposit while still retaining the resistance to penetration to the substrate afforded by double-layer nickel, triple-layer nickel coatings have been developed in which the semi-bright and bright layers are separated by a thin nickel layer electrochemically less noble than both of them. This thin layer of nickel, highly activated by incorporated sulphur, is described by Brown²³. Figure 13.9 shows a section through such a triple-layer coating. In service, corrosive attack is substantially confined to that part of the coating adjacent to the highly-activated layer.



Fig. 13.9 Triple-layer nickel deposit consisting of semi-bright and bright nickel layers with a thin, highly activated layer of nickel between them (after Reference 23)

Nickel coatings that induce microporosity in chromium topcoats In addition to the methods invoked in double- and triple-layer nickel coatings to ensure that the inevitable corrosion currents developed in a corrosive environment are directed away from the basis metal, another method of protecting the basis metal is to ensure that the conventional chromium top-coat ($0.3\text{ }\mu\text{m}$) is made sufficiently porous for the corrosion current to be dissipated over a large number of exposed nickel sites. This is achieved conveniently by applying, between the nickel coating and the chromium, a further thin nickel layer containing incorporated solid particles which are inert and which induce in the chromium a large number of pores. The rate of attack at any one pore is then small. Such coatings are increasingly used under severely corrosive service conditions and are described by Oderkerken²⁴ and Williams²⁵, among others.

Microcracked chromium topcoats Historically, microcracked chromium preceded the micro-porous chromium just described, but it is related to it in that the deposition conditions and thickness of the chromium topcoat are controlled to give porosity through a network of very fine cracks.

A thickness of at least $0.8\text{ }\mu\text{m}$ is normally needed to ensure that the required crack pattern is formed all over a shaped part. Such microcracked chromium coatings have a slightly lower lustre than the thinner conventional chromium deposits and take longer to deposit. The improved resistance to

corrosion that they impart to nickel coatings²⁶⁻²⁹ has been chiefly of interest to the automotive industry. In an attempt to avoid the slightly diminished lustre of thick microcracked coatings, an alternative process has been developed whereby a thin, highly stressed nickel layer is deposited upon the normal bright nickel layer. A conventional chromium topcoat is then applied, causing the thin nickel layer to crack, thereby cracking the chromium layer itself so as to give a microcrack pattern³⁰.

Supplemental films The Batelle Memorial Institute³¹ has developed a post-treatment for nickel plus chromium coatings in which the plated part is made cathodic in a solution containing dichromate. A film thereby formed on the surface seals pores in the coating through which corrosion of the nickel might otherwise occur. Later work³² suggests, however, that microcracked chromium gives superior results.

Control of quality of decorative nickel coatings Increasing international effort has been spent during the past few years in drawing up agreed recommendations aimed at ensuring that incorrect plating procedures do not diminish the high performance of nickel, or nickel plus chromium, coatings. During 1970, the International Standards Organisation issued Recommendation 1456 *Electroplated Coatings of Nickel plus Chromium* and Recommendation 1457 *Electroplated Coatings of Copper plus Nickel plus Chromium on Steel (or Iron)* which were used as guidelines by the British Standards Institution in drawing up BS 1224:1970 *Electroplated Coatings of nickel and Chromium* and BS 4601:1970 *Electroplated Coatings of Nickel Plus Chromium on Plastic Substrates*. These British standards specify the type and thickness of deposits required for various service conditions, appropriate accelerated corrosion test procedures, and methods of measuring other important properties. The quality of nickel salts and anodes for plating is specified in BS 558 and 564:1970 *Nickel Anodes, Anode Nickel and Salts for Electroplating*.

Engineering Electroplating

Engineering nickel coatings are used to improve load bearing properties and provide resistance to corrosion, erosion, scaling and fretting. The coatings are applied to new parts such as rolls for glass making, laundry plates, wire and tube. They are also used for reclaiming worn gears, shafts and other parts of buses and ships, and as undercoats for engineering coatings of chromium.

Deposits from Watts-type solutions Most coatings of nickel for engineering applications are electro deposited from a Watts-type bath³. Typical mechanical properties of deposits from Watts and sulphamate solutions are compared with those of wrought nickel in Table 13.15.

The uncertain effects of impurities are avoided by periodic or continuous electrolysis of the solution at low current densities to remove metallic contaminants and by filtration through active carbon to remove organic substances. A concise review of the effects of impurities and their removal is given by Greenall and Whittington³³.

Table 13.15 Typical mechanical properties of nickel deposits and wrought nickel

	<i>Appearance as plated</i>	<i>Hardness (H_V)</i>	<i>Ductility (% elongation)</i>	<i>Tensile strength (MN/m²)</i>	<i>Tensile stress (MN/m²)</i>
Hot rolled and annealed Nickel 200	—	90–140	47	460	—
Watts nickel	Dull, matt	130–200	25	420	150
Conventional sulphamate nickel	Dull, matt	160–200	18	420	14

The mechanical properties of Watts deposits from normal, purified solutions depend upon the solution formulation, pH, current density and solution temperature. These parameters are deliberately varied in industrial practice in order to select at will particular values of deposit hardness, strength, ductility and internal stress. Solution pH has little effect on deposit properties over the range pH 1.0–5.0, but with further increase to pH 5.5, hardness, strength and internal stress increase sharply and ductility falls. With the pH held at 3.0, the production of soft, ductile deposits with minimum internal stress is favoured by solution temperatures of 50–60°C and a current density of 3–8 A/dm² in a solution with 25% of the nickel ions provided by nickel chloride. Such deposits have a coarse-grained structure, whereas the harder and stronger deposits produced under other conditions have a finer grain size. A comprehensive study of the relationships between plating variables and deposit properties was made by the American Electroplaters' Society and the results for Watts and other solutions reported³⁴.

Hard nickel deposits When the plating variables are adjusted to give deposits with a hardness much above 200 H_V with a Watts solution, internal stress is usually too high and ductility too low for the deposits to be fully satisfactory. Higher hardness coupled with reasonable ductility can be achieved by addition of ammonium salts and operation at higher solution pH. A solution used for this purpose³⁵ and some deposit properties are as follows:

Composition

Nickel sulphate (NiSO₄·7H₂O): 180 g/l

Nickel chloride (NiCl₂·6H₂O): 30 g/l

Ammonium chloride (NH₄Cl): 25 g/l

Boric acid (H₃BO₃): 30 g/l

Operating conditions

Temperature: 60°C

pH: 5–6

Cathodic current density: 5 A/dm²

Deposit properties

Hardness: 400 H_V

Tensile strength: 1.1 GN/m²

Elongation: 6%

Values of hardness higher than 400 H_v (up to 600 H_v) can be obtained by addition of organic substances to a conventional Watts solution. Similarly, internal stress can be made less tensile, zero or compressive, by the use of organic addition agents of the type used in organic bright nickel solutions. In practice, such hard nickel deposits are seldom used in engineering applications unless the required coating is so thin that no machining will be required.

Increased hardness and wear resistance may also be achieved by incorporating approximately 25–50% by volume of small non-metallic particles. These may be carbides, oxides, borides or nitrides, and hardness values up to 560 H_v have been reported³⁶.

Deposits from sulphamate solutions The concentration of nickel ions in a conventional sulphamate plating solution is similar to that in a Watts solution, but nickel coatings deposited from the sulphamate bath have lower internal stress. Consequently higher plating rates than those employed in the Watts solution may often be used and this compensates for the higher initial cost of nickel sulphamate compared with nickel sulphate. Typical solution compositions and suitable operating conditions are given in Table 13.16 for the conventional solution and for a concentrated solution used for deposition at high rates:

Table 13.16 Typical solution compositions and suitable operating conditions for the conventional and the concentrated sulphamate baths

	<i>Conventional solution (g/l)</i>	<i>Concentrated solution (g/l)</i>
<i>Compositions:</i>		
Nickel sulphamate [Ni(NH ₂ SO ₃) ₂ ·4H ₂ O]	300	600
Nickel chloride (NiCl ₂ ·6H ₂ O)	30	10
Boric acid (H ₃ BO ₃)	30	30
<i>Operating conditions:</i>		
Temperature (°C)	25–50	60–70
Agitation	air	air
pH	3·5–4·5	3·5–4·5
Cathodic current density (A/dm ²)	2–15	2–80
Mean deposition rate (μm/h)	25–180	25–1 000

Replacement of nickel chloride by nickel bromide has been claimed³⁷ in the USA to reduce deposit stress, but subsequent German work³⁸ was unable to substantiate this finding.

Deposition of nickel at rates up to 1 mm/h in the concentrated solution is described by Kendrick³⁹. If pure nickel anodes are operated at a current density between 0·5 and 1·0 A/dm² in sulphamate solutions, a substance which behaves as a stress reducer is produced continuously in sufficient quantity that the stress in deposits can be varied at will from compressive to tensile by adjusting cathode current density and solution temperature. This finding is exploited with the concentrated sulphamate solution in the Ni-Speed process⁴⁰, and in a further development⁴¹ cobalt is added to give deposits of

hardness up to 500 H_v. The nature of the stress reducer conveniently produced at the nickel anode is unknown but it differs⁴² from the azo-disulphonate produced⁴³ at an insoluble anode such as platinum.

A comprehensive and authoritative study of the sulphamate bath has been made by Hammond⁴⁴.

Deposits from all-chloride solution Nickel deposits from a solution of nickel chloride and boric acid are harder, stronger and have a finer grain size than deposits from Watts solution. Lower tank voltage is required for a given current density and the deposit is more uniformly distributed over a cathode of complex shape than in Watts solution, but the deposits are dark coloured and have such high, tensile, internal stress that spontaneous cracking may occur in thick deposits. There is therefore little industrial use of all-chloride solutions.

Deposits from other solutions Nickel can be deposited from solutions based on salts other than the sulphate, chloride and sulphamate. Solutions based on nickel fluoborate, pyrophosphate, citrate, etc. have been extensively studied but none of them is used to any significant extent in Europe for engineering deposits.

Resistance to corrosion Oswald⁴⁵ has surveyed the resistance of engineering coatings of nickel to corrosion by various chemical environments. Environments in which nickel has proved satisfactory include: (a) dry gases including ammonia, the atmosphere, carbon dioxide, coal gas, fluorine, hydrogen, nitrous oxide; (b) carbon tetrachloride, cedar, creosote, hydrogen peroxide, mercury, oil, petrol, soaps, trichlorethylene, varnish; (c) alkalis (incl. fused), nitrates (incl. fused at 500°C), cheese, cream of tartar, eggs, fish, gelatin, fused magnesium fluoride, synthetic resins.

On heating in air, nickel forms a protective oxide and gives good service up to 700°C. Nickel is not recommended for exposure to chlorine, sulphur dioxide, nitric acid, sodium hypochlorite, mercuric or silver salts.

Where nickel is provided as a corrosion-resistant finish, a thickness of 120–130 μm is usually applied, but for well-finished basis metals and in mild environments, a lower thickness may be adequate. For parts machined after plating however, up to 0.5 mm may be required.

Effect of nickel coatings on fatigue strength In general, a coating of high fatigue strength raises the fatigue resistance of a basis metal having low fatigue strength, and vice versa. Thus nickel coatings applied to steels of tensile strength greater than about 420 MN/mm² can lead to reduced fatigue strength. In practice, this reduction in fatigue resistance is often taken to be negligible for industrial components because the safety factor used in design is high enough to accommodate the degree of loss⁴⁵. The loss can also be minimised either by using high-strength nickel deposits with compressive internal stress obtained by using appropriate addition agents, or by shot peening the surface of the steel before plating.

Effect on corrosion fatigue The combination of corrosion and fatigue can cause rapid failure, and a coating of nickel, by preventing corrosion, can increase the life of the parts. Figure 13.10 shows results obtained by the National Physical Laboratory on mild steel Wöhler specimens sprayed with

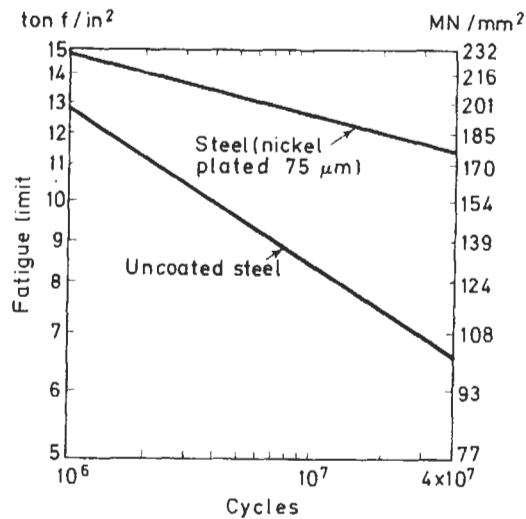


Fig. 13.10 Corrosion-fatigue tests; specimen sprayed with 3% sodium chloride (after Fescol Ltd.)

3% sodium chloride solution during testing at 2 200 cycle/min; the benefit given by the 75 μm nickel coating is clearly shown.

Effect on galling and fretting corrosion (Section 8.7) Even when well lubricated, nickel tends to gall, i.e. stick, when rubbed against some metals, including other nickel surfaces. Nickel also tends to give galling in contact with steel and it is necessary to chromium plate the nickel. Nickel does not form a good combination rubbing against chromium or against phosphor-bronze, owing to the action on the nickel of the hard particles contained in the phosphor-bronze. Good performance is given by well-lubricated nickel against normal white-metal bearings, brasses or bronzes.

When two metals in intimate contact are subjected to vibration, a dark powder forms at the areas of contact. The effect is referred to as fretting corrosion though it is due to wear rather than true corrosive attack. The galling effect between nickel and steel ensures good resistance to fretting corrosion and lubricated nickel against steel is a very satisfactory combination used widely in industry for components assembled by press-fitting.

Heat treatment after plating Heat treatment may be necessary after plating to improve the adhesion of coatings on aluminium and its alloys when certain processes, e.g. the Vogt process, are used, or to minimise hydrogen embrittlement of steel parts. Care is needed since heating may distort the part and impair the mechanical properties of the substrate.

Heat treatment to improve adhesion on aluminium and its alloys is normally carried out at 120–140°C for 1 h.

Heat treatment to minimise hydrogen embrittlement (Section 8.4) should be carried out immediately after plating and before any mechanical finishing operation. Delay is especially undesirable with steels having a tensile strength exceeding 1.4 GN/m². Steels with tensile strengths below 1 GN/m² are usually not heat treated. For the stronger steels, heat treatment is carried out

at 190–230°C for not less than 6 h with steels of tensile strengths in the range 1–1.85 GN/m², and for not less than 18 h in the case of even stronger steels.

Other aspects of engineering electrodeposited coatings A great deal of information has been published on important, but specialised, aspects of engineering nickel coatings.

General guidance is provided by BS 4758:1971 *Electroplated Coatings of Nickel for Engineering Purposes*⁴⁶. Cleaning, stopping off, etching, plating and subsequent machining of the coatings are discussed by Oswald⁴⁵, and the special pretreatments for maraging steels are described by Di Bari⁴⁷. Detailed recommendations for turning, grinding, milling and boring nickel coatings are given by Greenwood⁴⁸. Treatments that promote strong adhesion of subsequent nickel deposits after intermediate machining operations are discussed by Carlin⁴⁹. The physical and mechanical properties of nickel at elevated and sub-zero temperatures, determined with electroformed test pieces, have been described by Sample and Knapp⁵⁰. Other details of the properties of electrodeposited nickel coatings are given in Reference 51.

Electroless Nickel

In contrast to electrodeposited nickel, electroless nickel is deposited without application of electric current from an external supply. The metal is formed by the action of chemical reducing agents upon nickel ions in solution and, although several substances including hydrazine^{52–54} and its derivatives will give metallic nickel, commercial processes use either sodium hypophosphite which gives a nickel–phosphorus alloy, or, sodium borohydride or various alkyl aminoboranes which give a nickel–boron alloy. These reducing agents can be used in either batch or continuous deposition processes. The amount of boron (typically 3–7%) or phosphorus (usually 5–12%) incorporated in the deposits depends upon solution composition and deposition conditions, and it determines to a large extent the properties of the deposit.

A major advantage of the electroless nickel process is that deposition takes place at an almost uniform rate over surfaces of complex shape. Thus, electroless nickel can readily be applied to internal plating of tubes, valves, containers and other parts having deeply undercut surfaces where nickel coating by electrodeposition would be very difficult and costly. The resistance to corrosion of the coatings and their special mechanical properties also offer advantages in many instances where electrodeposited nickel could be applied without difficulty.

Commercial processes Commercial electroless nickel plating stems from an accidental discovery by Brenner and Riddell made in 1944 during the electroplating of a tube, with sodium hypophosphite added to the solution to reduce anodic oxidation of other bath constituents. This led to a process available under licence from the National Bureau of Standards in the USA. Their solutions contain a nickel salt, sodium hypophosphite, a buffer and sometimes accelerators, inhibitors to limit random deposition and brighteners. The solutions are used as acid baths (pH 4–6) or, less commonly, as alkaline baths (pH 8–10). Some compositions and operating conditions are given in Table 13.17⁵⁵.

Table 13.17 Brenner and Riddell electroless nickel solutions⁵⁵

	<i>Alkaline solution</i>	<i>Acid solutions</i>		
		1	2	3
<i>Composition (g/l)</i>				
Nickel chloride, NiCl ₂ ·6H ₂ O	30	—	30	30
Nickel sulphate, NiSO ₄ ·7H ₂ O	—	30	—	—
Sodium hypophosphite, NaH ₂ PO ₂ ·H ₂ O	10	10	10	10
Sodium acetate, NaC ₂ H ₃ O ₂ ·3H ₂ O	—	10	—	—
Sodium hydroxyacetate, NaC ₂ H ₃ O ₃	—	—	10	—
Sodium citrate, Na ₃ C ₆ H ₅ O ₇ ·5½H ₂ O	—	—	—	10
Ammonium chloride, NH ₄ Cl	50	—	—	—
<i>Operating conditions</i>				
pH	8–10	4–6	4–6	4–6
Temperature (°C)	90	90	90	90
Plating rate (µm/h)	7.5	25	12.5	5
Appearance	Bright	Rough, dull	Semi-bright	—

Further development was made by the General American Transportation Corporation, and their Kanigen process^{56,57} has been available since 1952. Other commercial processes based on the use of hypophosphite have since been developed. Work with reducing agents containing boron has given rise to the Nibudur process^{58,59} which has been available since 1965.

Plating on plastics Electroless nickel is used in thin deposits in order to provide an initial electrically-conducting surface layer in the preparation of plastics parts for electroplating. A typical procedure has as its first step an etching treatment of the plastic moulding in a solution of chromic and sulphuric acids in order to give a surface into which subsequent metallic deposits can key. The surface is then made catalytically active for electroless nickel deposition, usually by successive treatments in solutions containing tin compounds and compounds of a platinum group metal. Electroless nickel deposition is then followed by electrodeposition of the required coating which is usually copper plus nickel plus chromium.

Thorough rinsing between the pretreatment steps is essential to prevent carry-over of solutions. The commonest plastic plated is ABS (acrylonitrile butadiene styrene copolymer) but procedures are also available for polypropylene² and other plastics. In some proprietary processes, electroless copper solutions are used to give the initial thin conducting layer.

Engineering coatings In the field of engineering coatings of electroless nickel, use of boron compounds as reducing agents has up until now been confined largely to Germany. A comprehensive account of electroless nickel-phosphorus and nickel-boron plating in Germany was published by International Nickel⁶⁰. Electroless nickel-boron deposits have broadly similar mechanical, physical and chemical properties to those of electroless nickel-phosphorus deposits, and in the following discussion of deposit properties, data refer to nickel-phosphorus coatings unless otherwise stated.

Preparation of basis metals for plating Preliminary cleaning of various basis metals follows the broad principles used for electrodeposited nickel.

Electroless nickel deposition may then be carried out directly onto steel, aluminium, nickel or cobalt surfaces. Surfaces of copper, brass, bronze, chromium or titanium are not catalytic for deposition of nickel-phosphorus and the reaction must be initiated by one of the following operations:

1. Apply an external current briefly so as to electrodeposit nickel.
2. Touch the surface with a metal such as steel or aluminium while immersed.
3. Dip in palladium chloride solution (this gives only modest adhesion and carries the danger of contamination of the bath by solution carry-over).

Antimony, arsenic, bismuth, cadmium, lead, tin and zinc cannot be directly plated by these techniques and should be copper plated.

Resistance to corrosion Most authors who compare resistance to corrosion of electroless nickel with that of electrodeposited nickel conclude that the electroless deposit is the superior material when assessed by salt spray testing, seaside exposure or subjection to nitric acid. Also, resistance to corrosion of electroless nickel is said to increase with increasing phosphorus level. However, unpublished results from International Nickel's Birmingham research laboratory showed that electroless nickel-phosphorus and electrolytic nickel deposits were not significantly different on roof exposure or when compared by polarisation data.

Resistance to corrosion of electroless nickel, both as-deposited and, in most cases, after heating to 750°C, is listed by Metzger⁶¹ for about 80 chemicals and other products. Resistance was generally satisfactory, with attack at a rate below 13 $\mu\text{m}/\text{year}$. The only substances causing faster attack were acetic acid, ammonium hydroxide or phosphate, aerated ammonium sulphate, benzyl chloride, boric acid, fluorophosphoric acid, hydrochloric acid, aerated lactic acid, aerated lemon juice, sodium cyanide and sulphuric acid.

Electroless nickel-phosphorus should not be used with either fused or hot, strong, aqueous caustic solutions because the coating offers lower resistance to attack than does electrodeposited nickel. As-deposited electroless nickel-boron, however, offers good resistance to hot aqueous caustic solutions⁶⁰. It is also resistant to solutions of oxidising salts such as potassium dichromate, permanganate, chlorate and nitrate.

Heat treatment, e.g. 2 h at 600°C, improves the resistance to corrosion of nickel-boron and nickel-phosphorus electroless nickel deposits, especially to acid media. This presumably results from formation of a nickel-iron alloy layer⁶¹.

Mechanical properties

Ductility The ductility of electroless nickel deposits is low, but the brittleness of deposits containing less than 2% phosphorus can be reduced by heating to approx. 750°C for some hours followed by slow cooling.

Hardness The hardness of electroless deposits is higher after heating to intermediate temperatures, the final value depending upon temperature and time of heating. Values of maximum hardness of nickel-phosphorus after heating to various temperatures⁶¹ are plotted in Fig. 13.11; the variation of

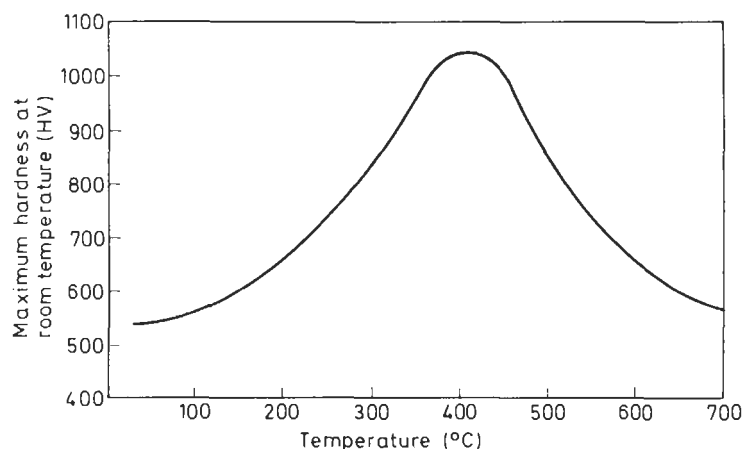


Fig. 13.11 Heat-treatment curve for electroless nickel (after Reference 61)

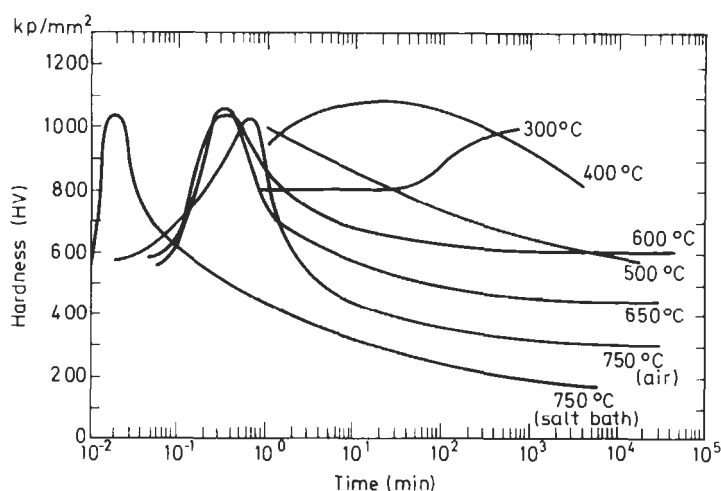


Fig. 13.12 Relationship between hardness and heat-treatment time for electroless nickel (after Reference 62)

hardness with heating time⁶² is shown in Fig. 13.12 for various heat-treatment temperatures. These curves show that hardness can be made to exceed 1 000 H_V by appropriate heat treatment. Nickel-boron deposits can similarly be heat treated to values up to 1 200 H_V .

Resistance to abrasion The resistance to abrasion of electroless nickel-phosphorus hardened to 600 H_V , assessed by Taber abrasion tests, has been found to be double that of electroplated nickel⁶³. However, electroless nickel coatings are not suitable for applications where two electroless nickel surfaces rub together without lubrication unless the values of hardness are made to differ by over 200 H_V units. Galling of aluminium, titanium or stainless steel may be overcome by applying electroless nickel to one of the two mating surfaces.

Applications

In 1970, according to best estimates, 60 000 t of nickel coatings were deposited in the western world. This figure corresponds to 13% of the nickel consumed for all purposes.

Decorative coatings It is impossible to give a comprehensive list of the uses of nickel coatings but applications of decorative nickel coatings, usually with a chromium top-coat, are given below:

1. Automotive: bumpers, grills, handles, over-riders, hubcaps, exhaust trim, locks, aerials, ash-trays, knobs.
2. Bicycles: rims, handlebars, spokes, cranks, hubs, bells, brake levers.
3. Perambulators: wheels, handles, springs, wing-nuts, body trim.
4. Door furniture: numbers, letter boxes, handles, bells, locks, keys.
5. Bathrooms: shower attachments, taps, chains, handles, locks, holders for soap and toothbrushes, mirror surrounds.
6. Kitchens: window fasteners, toasters, can-openers, trim for cooker, washing machine and dishwasher, clips.
7. General household: irons, needles, pins, press-studs, birdcages.
8. Tools: spanners, nuts, bolts, screws, screw-drivers, hacksaw bodies.

Toys, office equipment, sports equipment and shop furniture also provide large markets for decorative coatings of nickel or nickel plus chromium.

Engineering electrodeposits Engineering electrodeposits are used to give improved properties on new components, or to replace metal lost by wear, corrosion or mis-machining, or as an undercoat for thick chromium deposits.

For new components, the nickel coating is usually 25–250 μm thick. Normally, the deposits are not machined. Applications include pump bodies, laundry plates, heat exchanger plates, evaporator tubes, alkaline battery cases and food-handling equipment of various sorts.

Machined deposits on new equipment, including undercoats for chromium, are usually 125–500 μm thick. Applications include cylinder liners (on the water side), cylinders used in the rubber, pulp and paper handling industries, compressor rods and armatures for electric motors.

Machined deposits for salvaging worn parts, with or without a chromium topcoat, are limited in thickness only by the economic limitation when it becomes cheaper to manufacture a new part; thicknesses up to 5–6 mm are used. Applications include axles, swivel pins, hydraulic rams, shafts, bearings and gears. Among larger installations, the repair shop of the London Transport Executive at Chiswick houses many nickel plating tanks devoted to reclaiming worn engine parts from 8 000 buses, and repairs are carried out on about 15 buses each week.

Electroless nickel engineering deposits Electroless nickel is not usually deposited to thicknesses greater than about 125 μm . Where a greater total thickness is required, an electrolytic nickel undercoat should be used.

The number of applications has been growing at a considerable rate in recent years⁶⁰ and amongst the most common are hydraulic cylinders, tools for handling plastics, machine parts, printing cylinders, internal plating of valves and tubes, cooling coils, compressor housings, parts for pumps, storage vessels for chemicals, braking equipment, industrial needles, reaction

vessels, filters, moulds for glass, and precision gears. Electroless nickel is also used as a pretreatment stage in the preparation of some printed circuits⁶⁴.

Electroforms Electroforming is electrodeposition onto a suitable mandrel which is subsequently removed so that the detached coating becomes the desired product. The process has the advantages that an object of intricate form can be produced in a single stage, a variety of desired surface textures can be reproduced simultaneously, a high order of accuracy is obtained in reproducing mandrel shape, and tools can be replicated exactly for mass-production work. Nickel has the particular advantages that its internal stress, hardness and ductility can be varied at will between wide limits and the final electroforms are strong, tough and highly resistant to abrasion, erosion and corrosive attack. The many applications of electroforming with nickel in Europe have recently been reviewed by Bailey, Watson and Winkler⁴².

Recent Developments

Decorative Plating

There has been continuing progress in recent years in the formulation of proprietary nickel electroplating solutions. Bright nickel processes are available with improved brightness and levelling on unpolished substrates, improved ductility, and with brightness obtained over a wider range of current densities. Wearmouth and Bishop⁶¹ have developed a process for applying a pattern to decorative nickel plus chromium coatings after plating, by laying a stencil over the surface and exposing the bare areas to the peening action of a slurry of glass beads in water to form a satin texture. Microcracking of the chromium occurs over the satin regions and resistance to corrosion is thereby improved.

New pretreatments for aluminium to enable it to be nickel plated more easily have led to novel decorative applications including large mirrors. Wyszynski⁶⁶ has described a proprietary process applicable to a wide range of aluminium alloys.

Concern over the health hazards of the hexavalent chromium solutions used to form the top coat of conventional nickel plus chromium coatings have encouraged research into trivalent chromium plating solutions. A process with better throwing power and improved covering power than those of hexavalent chromium has been described by Smart *et al.*⁶⁷. A process for depositing a chromium-iron, or chromium-nickel-iron alloy, has been outlined by Law⁶⁸.

Engineering Electroplating

Wearmouth⁶⁹ has described the production of nickel-cobalt, nickel-manganese, and nickel-chromium alloy coatings for non-decorative uses. The nickel-cobalt and nickel-manganese are electrodeposited direct from sulphamate-based solutions, the nickel-cobalt alloys offering higher hardness than the nickel-manganese alloys, which are restricted to a relatively

low manganese content. However, the manganese prevents embrittlement on heating that would otherwise arise from sulphur incorporated in the plating from conventional sulphur-bearing organic additives in the plating solution. The nickel-chromium alloys are formed by incorporating chromium carbide in nickel electrodeposit, followed by heat treatment in hydrogen at 1 000°C to decompose the carbide.

Composite Coatings

A wide range of applications for hard, wear-resistant coatings of electroless nickel containing silicon carbide particles have been discussed by Weissenberger⁷⁰. The solution is basically for nickel-phosphorus coatings, but contains an addition of 5–15 g/l silicon carbide. Hübner and Ostermann⁷¹ have published a comparison between electroless nickel-silicon carbide, electrodeposited nickel-silicon carbide, and hard chromium engineering coatings.

Electroless nickel coatings containing PTFE particles have been discussed by Tulsi⁷², and non-stick coatings of electrodeposited nickel containing 30% by volume PTFE particles are described by Naito and Otaka⁷³. They found that the addition of organic additives to increase the hardness of the nickel matrix to 500–600 H_v reduced the incorporation of the PTFE to 10–15% by volume.

Electroforming

Nickel Foil Jones and McGrath⁷⁴ have described the continuous electrodeposition of nickel on to a rotating titanium drum, and detachment of the nickel coating to give a process for manufacturing foil up to 500 mm wide. The foil is used directly as an intermediate layer in fire-resistant blankets on North Sea oil rigs and as the substrate for graphite gaskets employed in high-temperature applications, where the nickel replaces asbestos. The main use, however, is as a foil 0.013 mm thick carrying a solar energy absorbing surface. For this purpose, the foil is coated with a thin black mixed nickel oxide layer which out-performs conventional nickel-black (an electrodeposited zinc-nickel sulphide complex) and chrome-black coatings. A significant advantage of the foil approach is that the foil can be fixed adherently on to a variety of collector surfaces and shapes that could not be electroplated and blackened directly. This solar foil is already used in 25 countries in Europe, North and South America, and Asia. Other uses for nickel foil include printed circuits where welded, instead of soldered, connections are specified, in heating elements for panel heaters, and in the manufacture of bursting discs and explosion release devices⁷⁵.

Abrasive Sheets Abrasive sheets, polishing and lapping foils are electroformed in nickel using a photoresist technique⁷⁵. The sheets bear tiny cutting edges all at the same level and have almost a planing effect when rubbed against the surface to be worked. The nickel is hardened to 600 H_v and the spaces between the cutting edges have a mirror-like finish to minimise retention of abraded material which could otherwise clog the surface.

Tubes and Perforated Tubes Electrodepositing nickel non-adherently all over the curved surface of a cylinder, and then sliding off the coating, produces a tubular nickel product. Some tubes manufactured in this way are plain, but most are perforated. They are used industrially for screen printing textiles, carpets and wall paper⁷⁵.

Bands and perforated bands Detached nickel coatings in the form of bands are made by a similar technique to that used for tubes except that their diameter is usually greater and their width much less. The outside layer of nickel can itself be an integral coating comprising the nickel matrix and incorporated diamonds. Such bands are used as cutting tools⁷⁵. Some practical aspects of the incorporation of the diamonds in nickel have been published⁷⁶⁻⁷⁷. Electroformed nickel perforated bands are used in cigarette making machines to transport the shredded tobacco at a constant rate. Since the bands contain no joins, they resist fatigue and have long service life⁷⁵.

Bellows Nickel bellows can be made by electrodeposition onto a grooved cylinder. In this case, the nickel coating cannot be slid off, and so the substrate must be removed destructively. The grooved cylinders or mandrels are frequently of aluminium alloy which is dissolved away in caustic alkali when the nickel deposition is completed. Uses include pressure switches, flexible couplings, and pressure transducers⁷⁵.

Discs Discs of nickel electroformed on to mandrels bearing grooves modulated with recorded sound have been used for many years for stamping sound recording discs. This process has been adapted and refined for the manufacture of digital records, including video discs^{78,79}. Video disc stampers must be hard, stress-free, and flat to within 0.1 μm ; results of a short investigation directed towards these requirements have been reported⁸⁰.

Other applications of nickel electroforms are reviewed in Reference 75.

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13.8 Chromium Coatings

It is not economically or technically feasible to use chromium in a fabricated form, but the high resistance of the metal to corrosion can be utilised by applying a thin coating of chromium to less resistant metals. Although the metal is base ($E^\circ_{\text{Cr}^{3+}/\text{Cr}} = -0.74 \text{ V (SHE)}$) it is protected by a thin, stable, tenacious, refractory, self-sealing film of Cr_2O_3 . This is preserved by oxidising conditions, and the metal is very resistant to high-temperature oxidation and to atmospheric exposure in most natural environments. Unlike silver and copper, it is not tarnished by hydrogen sulphide, nor is it 'fogged' like nickel by atmospheres containing sulphur dioxide.

The high reflectivity, pleasing blue-white colour, and the oxidation- and tarnish-resistance of the metal are the main reasons for its application in the form of thin coatings to cheaper and less resistant metals, for decorative purposes.

In addition, the extreme hardness of the metal, its low coefficient of friction and its non-galling property, combined with its corrosion resistance, make it particularly valuable as a coating where resistance to wear and abrasion are important. Thick deposits applied for this purpose are referred to as *hard* chromium to distinguish them from the thin decorative deposits.

Methods of Applying Chromium Coatings

The only methods of significance for producing chromium coatings are electrodeposition, chromising and vapour deposition. The last-mentioned is used only to a negligible extent for special high-temperature applications, as the coatings are less porous than electrodeposited chromium and are less liable to spall (see Section 12.5). The metal is deposited *in vacuo* from chromous or chromic iodide. Chromising produces coatings which are essentially alloys, and which are considered in Section 12.3. Electrodeposited chromium is one of the most widely used metallic coatings.

Electrodeposition (Section 12.1)

Electrodeposited chromium, both decorative and 'hard', is produced with the use of a solution of chromic acid containing a small amount of catalyst which is usually sulphuric acid, although fluosilicic or fluoboric acid may be used. A typical electrolyte contains 250–400 g/l of chromic acid and

2.5–4.0 g/l of sulphuric acid; the $\text{CrO}_3:\text{SO}_4^{2-}$ ratio is important and for satisfactory plating it should be maintained at about 100:1. If the catalyst content is too low no metal will be deposited, and if it is too high throwing power will be considerably reduced. The cathode efficiency is usually only 10–12% although up to 20% can be achieved with a silicofluoride catalyst. The evolution of hydrogen at the cathode and oxygen at the anode (6% antimonial-lead, which becomes coated with lead peroxide) necessitates provision for removal of the toxic spray by extraction or for the suppression of bubble formation by the addition to the baths of a perfluoro-carbon type of surface-active agent, the only type known to be stable under the prevailing conditions¹. The chromium content of the bath is replenished by addition of chromic acid, as a chromium anode is not technically feasible.

The voltage used is 4–8 V, current density 9–22 A/dm², and temperature 38–43°C. Higher current densities, up to 55 A/dm², are used for thick deposits. A considerable amount of heat is generated during electrodeposition and provision must be made for cooling of the electrolyte during operation.

The covering and throwing power of the electrolytes is low, and bright plating which is required for decorative purposes can be obtained for a given composition and temperature only within a relatively narrow range of current densities. Outside this range, the deposits are not bright and the hardness of chromium is such that polishing is very difficult and uneconomical. Hence special care must be taken in the racking of irregularly shaped articles to avoid unplated areas, or dull and burnt deposits.

Rack design is important in obtaining uniform deposits and good coverage in view of the low efficiency of the bath. The use of computer modelling has been examined for this purpose³⁵.

Much attention has been given of late to the development of chromic acid baths with higher efficiencies, especially for hard chromium plating, since it is here that the greatest potential for savings in time and energy can be achieved (see below). Amongst the addition agents which have been found to be effective in increasing the efficiency of the conventional chromic acid solution are the bromates, iodates and dichloromalononic acid³⁶. Several commercial high efficiency baths are currently in use.

Self regulating chromium The self-regulating chromium solutions were introduced to eliminate the need for maintaining the correct catalyst concentration by periodic analysis; they depend on the addition of a sparingly soluble sulphate to the bath which supplies the correct amount of SO_4^{2-} automatically. Initially strontium sulphate (solubility approx. 1.75 g/l at 30°C and 21 g/l at 40°C) was employed for this purpose². The strontium sulphate forms a layer on the bottom of the bath, which must be stirred from, time to time. A bath with a CrO_3 concentration of 250 g/l would have a catalyst content of 1.52 g/l SrSO_4 and 4.35 g/l of K_2SiF_6 . Potassium dichromate and strontium chromate have also found application as additives for the control of the saturation solubility of the catalyst.

Succinic acid has also been proposed³ for the stabilisation of a self-regulating bath, a recommended bath composition consisting of 375 g/l of CrO_3 , 8 g/l of SrSO_4 , and 40 g/l of succinic anhydride; the bath is

operated at 35°C. Self-regulating solutions generally have a higher current efficiency (18–25%) than the conventional bright solutions⁴.

Tetrachromate electrolytes The alkaline tetrachromate baths are used to a small extent chiefly for the direct chromium plating of zinc die-castings, brass or aluminium, since the solutions do not attack these metals⁵. The original bath was developed by Bornhauser (German Pat. 608 757) and contained 300 g/l of chromic acid, 60 g/l of sodium hydroxide, 0.6–0.8 g/l of sulphuric acid and 1 ml/l of alcohol.

The essential constituent of the bath is sodium tetrachromate, $\text{Na}_2\text{Cr}_4\text{O}_{13}$, which is, however, only stable at temperatures below about 25°C. This temperature should therefore not be exceeded in the operation of the bath. Current densities of 75–150 A/dm² are used. The current efficiency of the bath is high (30–35%) so that the metal is deposited at the rate of about 1 µm/min. The deposits are normally matt in appearance, but are comparatively soft and readily polished.

A proprietary tetrachromate bath has been used in Germany under the name of the *D* process⁶. By the use of additions of magnesium oxide and sodium tungstate it is claimed that the current efficiency of the bath can be raised to as high as 35–40%. Other additives such as indium sulphate, sodium selenate or sodium hexavanadate enable bright deposits to be obtained.

Trivalent chromium baths Considerable attention has been given recently to the possibility of depositing chromium from trivalent chromium solutions. One bath uses a dimethyl formamide–water solvent system having chromic chloride as an active salt with additions of ammonium chloride, sodium chloride and boric acid to improve current efficiency and conductivity. Plating efficiencies are of the order of 30–40% based on Cr(III) and bright deposit can be obtained over the normal plating range of 25–1.25 A/dm² at a plating speed of at least 0.3 µm/min. The deposits are micro-discontinuous^{7–10}.

A commercial trivalent chromium bath which is entirely aqueous and based on chromic sulphate (Cr_2O_3), with complexing agents, conductivity salts, a buffer (e.g. boric acid) and a wetting agent, has been introduced and has had some success³⁷ although it has the disadvantage of having to be operated in a diaphragm cell. The deposit has a more greyish colour than that obtained from a chromic acid bath, and has a lower hardness. The bath is mainly used for decorative purposes, being unsuited to producing thicker coatings.

The attractions of trivalent baths are their lower toxicity, greater efficiency, and a considerably simplified procedure for efficient treatment.

Properties of electrodeposited chromium

Structure Although massive chromium has a body-centred cubic structure, electrodeposited chromium can exist as two primary modifications, i.e. α - (b.c.c.) and β - (c.p.h.). The precise conditions under which these forms of chromium can be deposited are not known with certainty. Muro¹¹ showed that at 40°C and 2.0–22 A/dm² the deposit was essentially α -chromium but small amounts of β - and γ - were present, while Koch and Hein¹² observed

the β - form at 50°C and 40 A/m². This form is unstable, however, and is converted rapidly by heating or more slowly by storage at room temperature to the α - form.

The crystal structure is exceedingly fine and cannot be revealed by the microscope; Wood¹³ has shown by X-ray diffraction that the grain size is 1.4×10^{-9} m.

Porosity and discontinuities Chromium plate of 0.5 μ m or less in thickness is invariably porous. An increase in thickness above this value, however, when plating is carried out under conventional conditions (i.e. 38–43°C, 11–16 A/dm² and a CrO₃:SO₄²⁻ ratio of 100:1 to 120:1) results in a cracked deposit which can be revealed by microscopical examination at about $\times 350$ magnification. Cohen¹⁴ considers that the cracks are filled with a transparent film, probably of hydrated chromic oxide, which dehydrates on heating to form Cr₂O₃. According to Snavely¹⁵, cracks and included material in the cracks are caused by the formation of unstable chromium hydrides during plating. A hexagonal form of the hydride (CrH to CrH₂) is formed initially, but decomposes spontaneously to α -chromium and free hydrogen. This involves a decrease in volume of over 15%, and since the plate is restrained by the basis metal, surface cracks form normal to the surface. The chemical constituents found in the electrodeposit are due to the drawing of electrolyte into the cracks, which are then covered over by subsequent layers of electrodeposit.

Black chromium plating Black chromium deposits are frequently required for the optical and instrument industries. The deposits contain large amounts of chromium oxides and are not strictly speaking chromium deposits. Graham¹⁶ recommends a solution consisting of 250 g/l of chromic acid, 0.25 g/l of hydrofluosilicic acid and a CrO₃:H₂SiF₆ ratio of 1 000:1. The bath is operated at about 32°C with a current density of about 30 A/dm² and a bath voltage of 6 V. The electrolyte solution must be free from sulphuric acid, excess sulphate ions being removed by treatment with barium sulphate. Silvery deposits of chromium containing some nickel are obtained at 70–100 A/dm² from a bath consisting of 200 g/l of chromic acid, 20 g/l of nickel chloride and 5 ml/l of glacial acetic acid. By a short immersion (5–30 s) in concentrated hydrochloric acid, the deposit becomes greyish black. Good black deposits are produced from a bath containing 200 g/l of chromic acid, 20 g/l of ammonium vanadate and 6.5 ml/l of glacial acetic acid at a current density of 95 A/dm² and a temperature of 35–50°C¹⁷. Some types of black chromium deposits are claimed to have very good corrosion resistance.

Hard chromium plating The so-called 'hard' (or thick) chromium deposits are applied on carbon and alloy steels, cast iron and light alloys, to improve resistance to wear, abrasion and corrosion. The solutions employed generally contain 150–500 g/l of chromic acid and employ a CrO₃:H₂SO₄ ratio of 80–120. Deposit thicknesses of 12–150 μ m are applied, but the use of thicker deposits is limited to parts which are not subject to bending or stress. Plastic moulds are generally plated with coatings of 10–15 μ m, which are considered adequate. Hard chromium deposits are normally ground or lapped before being put into service, and allowances must be made for this

operation to be carried out. Applications for hard chromium deposits include cylinder liners, crankshafts, pump shafts, plastic moulds, dies, cams, rockers, journals and bearings.

Plating is carried out by suspension in the bath in the usual manner, areas which are not to be plated being protected by 'stopping off' materials, such as lacquers, waxes or plastics. Chromium can also be deposited locally without the use of a tank by the tampon method. The Dalic¹⁸ process makes use of an insoluble anode and an absorbent pad containing the electrolyte solution, which is a slightly alkaline organic complex amino-oxalate compound of chromium dissolved in an alcohol, with a wetting agent added. High current densities are used, and rates of deposition of up to $2.5 \mu\text{m}/\text{min}$ are practicable. The deposit is slightly softer than the conventional hard chromium deposits.

A trivalent hard chromium bath has recently been described³⁸. The bath contains potassium formate as a complexing agent, and thicknesses in excess of $20 \mu\text{m}$ can be deposited. Hardnesses of up to 1650H_V can be obtained by heat treatment at 700°C . The deposits contain 1.6–4.8% carbon, and the bath is suitable for the deposition of composite deposits containing diamond or silicon carbide powder.

Several high-efficiency hard chromium plating baths are now available commercially. A solution which does not contain fluoride, and does not therefore attack steel or aluminium, has been described by Schwartz³⁹. At $50 \text{ A}/\text{dm}^2$ and 53°C the cathode efficiency is about 25%, enabling deposition to be carried out at the rate of $1 \mu\text{m}/\text{min}$, with a consequent substantial saving in power and time. The deposit is bright, and has a hardness of about 1050H_V .

Hard chromium plating provides excellent resistance to atmospheric oxidation both at normal temperatures and at temperatures of up to 650°C . It is unattacked by many chemicals, owing to its passivity. When attack takes place, this usually commences at cracks in the chromium network; hence the most corrosion-resistant deposits must have a very fine structure, such as is obtained from relatively high solution temperatures using low current densities.

Corrosion

Electrodeposited chromium, if it is required to protect an underlying metal against corrosion, has to be applied in considerable thicknesses, owing to its high porosity and tendency to crack. Such deposits are expensive to produce and are not fully bright, and, as the polishing of chromium is difficult, it is the general practice to use a protective undercoat, usually nickel, when ferrous or non-ferrous metals have to be protected. For wear resistance or engineering applications, however, 'hard' chromium coatings are usually plated directly on to steel and other metals at thicknesses of up to approximately 0.50 mm as against 0.00025 – 0.002 mm for decorative chromium deposits on a nickel undercoat.

When corrosion of a chromium-coated metal takes place, the corroding current concentrates its action on fissures in the deposit. There appears to be an incubation period, after which rapid attack occurs in the form of pits, and

sometimes a network of corrosion can be observed. The chromium becomes cathodic, the underlying metal (usually nickel) which is exposed at the pores or stress cracks of the chromium plate being anodic (see Fig. 13.13).

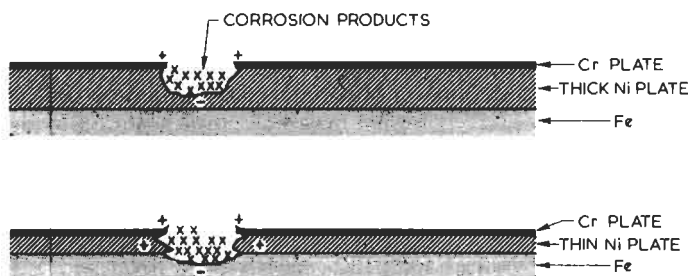


Fig. 13.13 Two stages in the corrosion commencing at a discontinuity in the chromium plating (after *Electroplating and Metal Finishing*, 12 No. 1, 3 (1959))

Dettner¹⁹ claims that the degree of polish of the base metal has a definite influence on the corrosion resistance of chromium deposited directly on steel, a high degree of polish leading to improved protection; electrolytic polishing is said to lead to particularly good durability²⁰. Polishing of the chromium layer usually has little effect, but excessive heat generation can lead to reduced corrosion resistance. It is desirable, from a practical point of view, that the chromium be deposited within the bright plating range, and although this does not always coincide with the conditions necessary for maximum protection, a reasonable compromise can be reached.

Crack-free Chromium

As has already been stated, attempts to reduce the porosity of chromium plating by increasing its thickness much above 0.0005 mm result in cracked coatings when normal solutions and conditions are employed. It is, however, possible to obtain crack-free deposits in thicknesses up to 0.0025 mm, with a consequent improvement in corrosion resistance as shown by accelerated tests, by the operation of the bright chromium plating bath at 49–54°C, and higher $\text{CrO}_3:\text{SO}_4^{2-}$ ratios of 150:1 to 200:1^{21–23}. Crack-free deposits can be obtained under conditions outside these ranges, but for practical operation these are the ones which it is most convenient to employ.

The main drawback to plating chromium under these conditions is that the current requirements are greater owing to the need to work at twice or three times the conventional current density. There is also some tendency for the deposit to be rather more blue in colour, while frostiness can develop at high-current-density areas. Better results can be obtained by allowing the work to enter the plating tank at a lower voltage (2–3 V) before applying the full plating voltage, or by working at a temperature of around 49°C.

Some confirmation of these findings has been reported by Safranek *et al.*²⁴ in their work on the corrosion resistance of plated die-castings. They found that 0.00064 mm (minimum) of bright crack-free chromium

deposited in a high-ratio bath at 54°C will extend the 'corrosion-free' life of plated die-castings in highly corrosive environments to at least one year, as compared with less than six months for normal deposits. Bright, crack-free chromium deposited on 0.0076 mm of copper and 0.020 mm minimum of bright nickel furnished good protection against accelerated corrosion.

Deposits of more than around 0.0020 mm in thickness cannot be applied in this way without the initiation of cracks visible to the naked eye particularly at high-current-density areas. This is a disadvantage, since owing to the poor 'throw' of chromium it is sometimes necessary to exceed this thickness at such areas on articles of complex shape in order to secure an adequate deposit in recesses. A method of overcoming this problem known as *duplex* chromium plating (see below) has been developed.

Using pulse plating techniques with a duty cycle of 50%, it is also possible to produce crack-free chromium deposits from a sulphate- or silicofluoride-catalysed solution with a hardness similar to deposits obtained by direct current⁴⁰. A high frequency (2 000–3 000 Hz) is required to give the hardest deposits at a current density of 40 A/dm² and a temperature of 54°C. It is important to avoid conditions that will co-deposit hydrides.

Microcracked Chromium

Duplex Chromium

It has been claimed that better corrosion protection than that afforded by the high-temperature chromium-plating method can be obtained by the use of a double chromium plate. In this system, bright crack-free chromium is deposited as described above, followed by an equal thickness of a bright, finely cracked chromium plate. The total chromium thickness should be not less than 0.00075 mm, and should preferably be greater. The initial crack-free deposit may be obtained by plating from a solution of chromic acid and sulphuric acid (250–400 g/l of chromic acid, chromic acid to sulphate ratio 125 to 175:1), operating temperature 49–54°C. Baths containing fluoborates, which are self-regulating so far as the ratio of chromic acid to catalyst is concerned, can also be used successfully for producing crack-free deposits²⁵.

Immediately after this deposit has been plated, a cracked chromium layer is applied from a dilute bath containing about 200 g/l of chromic acid at 46–52°C. The articles to be plated should enter the bath at a low voltage to prevent streakiness. Fluoboric or fluosilicic acid in the bath, in addition to sulphuric acid, helps to produce the required fine stress cracking.

Single-layer Chromium

A number of proprietary solutions are now available for producing the same result from a single bath. The plating time tends to be rather longer, but this can be reduced either by increasing the current density (which may upset the crack pattern), by decreasing the chromium thickness at which cracking occurs, or by increasing the cathode efficiency.

The effect of the finely cracked chromium layer is to equalise the anode and cathode areas more nearly, so that corrosion of the nickel under the chromium takes place more slowly than it would at larger, isolated cracks. Moreover, the corrosion proceeds laterally along the nickel surface and not in depth as is the case with conventional chromium; hence failure of the coating under adverse conditions is less likely to occur.

A crack count of 30–80 cracks/mm is desirable to maintain good corrosion resistance. Crack counts of less than 30 cracks/mm should be avoided, since they can penetrate into the nickel layer as a result of mechanical stress, whilst large cracks may also have a notch effect²⁶. Measurements made on chromium deposits from baths which produce microcracked coatings indicate that the stress decreases with time from the appearance of the first cracks²⁷. It is more difficult to produce the required microcracked pattern on matt or semi-bright nickel than on fully bright deposits²⁸. The crack network does not form very well in low-current-density areas, so that the auxiliary anodes may be necessary.

Corrosion tests have shown that a system based on copper, double nickel and microcracked chromium gives good corrosion resistance, although automobile parts plated with microcracked chromium are not as easy to clean as those plated with crack-free chromium deposit.

Microporous Chromium

One of the best methods of improving the corrosion resistance of nickel-chromium deposits is to apply a uniformly porous layer, rather than a microcracked chromium layer, this having the advantage that the microporosity is not greatly dependent on the current density at which the chromium plating is carried out. Hence the chromium can be deposited in microporous form on quite complex-shaped articles from a single, conventional chromium solution. The method of achieving this is to suspend inert particles in the underlying nickel coating; the presence of these, being non-conducting, results in the formation of a highly microporous chromium deposit. Severe electrochemical attack of the underlying nickel at large cracks or pores in the chromium is thus prevented, and a substantial improvement in the corrosion resistance of the combined coating is obtained. A relatively thick copper deposit (75 μm) underneath the nickel layer has been found to add considerably to the protective value of the coating. Thereafter very little improvement occurs. The large number of microscopic anode nickel sites which develop when about 0.25 μm of chromium is applied results in very weak corrosion currents with extremely low corrosion penetration. The number of pores in the chromium can be varied from about 3 000 per square centimetre to several million per square centimetre²⁹. The variation in the porosity of microporous chromium with thickness is shown in Fig. 13.14.

In practice a special nickel solution containing the suspended particles is applied over the normal bright nickel deposit. The plating time in this solution is from 20 s to 5 min; the most suitable ratio of the two deposits has to be determined in each particular case.

The use of a chromium deposit with a fine porosity pattern of 15 000 to 45 000 pores per square centimetre in the usual thickness results in a sharp

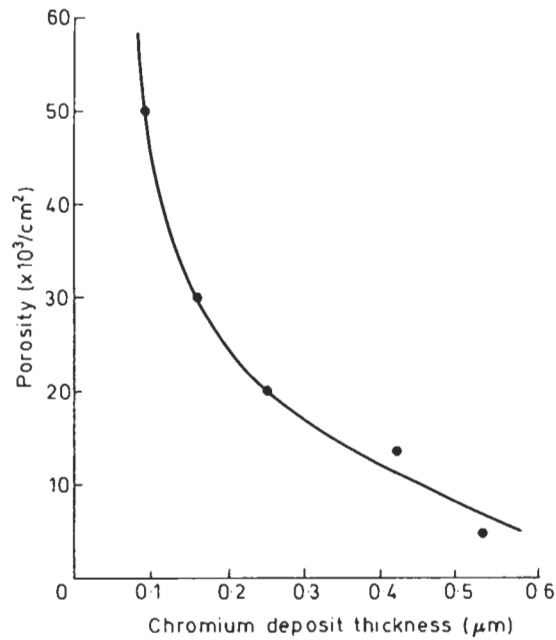


Fig. 13.14 Variation of porosity of microporous chromium with thickness of deposit

slowing down of the corrosion rate. Such corrosion as does occur develops laterally, thus very greatly delaying the downward penetration into the vulnerable base metal (Fig. 13.15).

Since the theory of the mechanism of the microporous chromium system depends on the fact that the occlusions in the underlying nickel provide a

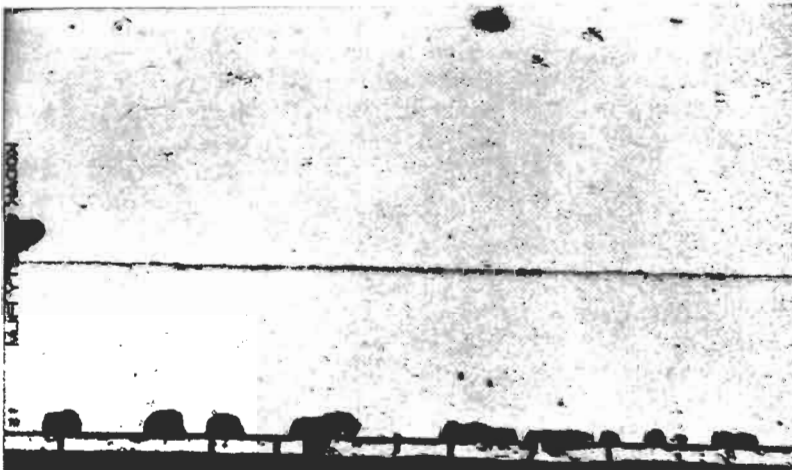


Fig. 13.15 Lateral corrosion in nickel deposit layer containing inert particles beneath microporous chromium

large number of sites where nickel can be corroded at discontinuities in the nickel deposit, it was at one time believed that increasing the chromium thickness excessively would be disadvantageous, as it would seal some of the active nickel sites. Carter³⁰ has shown that this is not the case provided that the porosity in the chromium is not reduced below about 15 000 pores per square centimetre. When copper was present under the nickel plus chromium coating, full protection of steel was obtained in industrial atmospheres for two years in all environments. This effect on copper is not found under conventional chromium coatings. The reason for this is ascribed to the fact that the copper remains cathodic to the nickel because of the large area of nickel involved in the corrosion reaction when the chromium layer is discontinuous³¹. With conventional deposits, however, the smaller area of the corroding nickel allows high current densities to occur in the pits so that the copper becomes anodic and is readily penetrated. The effect is reduced when the nickel layer adjacent to the copper is of a less corrodible type (i.e. semi-bright, dull nickel) and hence the advantages of the copper undercoat are less in the systems employing double nickel deposits. There is some deterioration or dulling in the appearance of articles plated with microporous chromium (as is also the case with the microcracked deposits), but this is only significant on exposure in the severest environments. Dulling was progressively reduced by increasing thickness of the chromium deposit within the range studied, without adverse effect on the protection of the basis metal.

Chromium–nickel–chromium

A further development is the use of a combined chromium–nickel–chromium or nickel–chromium–nickel–chromium deposit on steel- or zinc-base alloy articles³². An advantage of this system is that the first chromium layer need not be plated within the bright range of the chromium bath, so that plating can be carried out under conditions giving deposits of maximum corrosion resistance; such conditions do not coincide with those under which fully bright chromium plate is obtained.

Knapp³³ reports that a chromium deposit of 0·000 25 mm from the usual type of chromium bath, followed by 0·013 mm nickel and a further 0·000 25 mm of chromium gave protection equal to that of a nickel coating of double the thickness applied in the form of normal nickel and chromium plate.

Porous Chromium

Porous chromium is largely used on cylinder liners for automobile engines, its advantage being that it retains lubricants better than normal chromium³⁴. The porosity is usually created by etching the metal. Appropriate etching methods include reversal of current to make the work anodic in the plating solution, and cathodic or chemical treatment in a separate bath. Hydrochloric, sulphuric or oxalic acid may be used as the etching electrolyte in a separate bath, the work being made cathodic; alternatively, chemical etching

without current in a hot dilute sulphuric acid or hydrochloric acid bath, to which an inhibitor such as antimony oxide is added, can be employed. Whether pin-point or channel porosity is produced depends primarily on the conditions of deposition, solution temperature and composition being the principal factors. Generally, higher temperatures and higher sulphate ratios in the bath favour channel-type porosity. The degree of porosity must be carefully controlled in order to ensure that excessive roughness is not produced. The ideal condition is one where the chromium becomes adequately receptive for oil but remains smooth. It is usual to hone or lap the porous chrome; careful cleaning is then essential to remove the debris produced by honing.

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13.9 Noble Metal Coatings

The most widely used methods for the application of coatings of gold, silver and the platinum group metals (platinum, palladium, rhodium, iridium, ruthenium, osmium) to base metals are mechanical cladding and electroplating.

In cladding, the coating is applied in the form of sheet, which may be bonded to the underlying metal by brazing or by elevated-temperature working processes such as swaging and drawing for the production, for example, of platinum-clad molybdenum or tungsten wire, or hot-rolling followed by spinning, cupping or drawing, for the production of coated dishes, tubes, etc. Silver coatings are extensively applied in this way in the lining of chemical reaction vessels, distillation and evaporation equipment, etc. particularly in fine chemical manufacture and food processing where product purity is vital and the protective coating must therefore be completely impervious. The main advantage of silver in this type of application, apart from its relative cheapness as compared with other metals of the group, is its good resistance to organic acids and other compounds and to chloride-containing media. Its high heat-transfer capacity is also a useful asset. Platinum and gold find application in a similar sense where particular conditions warrant their cost. Coating thicknesses may vary from less than 0.025 mm to 0.640 mm, depending on service requirements.

Palladium can be applied in the same way, but is not employed to a significant extent in this form since its corrosion resistance is inferior to that of platinum. Application of other metals of the platinum group, i.e. rhodium, ruthenium and iridium, as protective claddings is hindered by limitations in working technology. In experimental work on the protection of soldering iron bits by ruthenium, the expedient has been adopted of fabricating small hollow cones by compacting and sintering ruthenium powder, and fixing these to the tips by brazing¹.

In the case of silver and gold, thick coatings of equivalent protective value to those produced by cladding can be obtained by electrodeposition; both metals have, in fact, been successfully employed for electroforming. In the more general case, however, electrodeposited coatings, particularly those of the platinum group metals and, to a lesser extent, gold plated in the bright condition, are subject to some degree of porosity and, with increasing thickness, to the possibility of spontaneous cracking due to internal stress in the as-deposited condition. Nevertheless, the bulk of precious metal coatings used for decorative and industrial purposes, including tonnage use in the electronics field, are applied by electroplating, since protective requirements,

though arduous, are in most cases less critical than those demanded by long term exposure to liquid or high-temperature corrosive environments, and some degree of porosity can often be tolerated.

Processes for electrodepositing silver, gold, platinum, palladium and rhodium have been long established. In this group the most striking development of recent times has been the emergence of bright gold plating solutions which utilise the stability of gold cyanide at relatively low pH values to plate under acid conditions^{2,3}, and more recently still, of noncyanide electrolytes based on sulphite complexes⁴. Relatively new electrolytes have also been formulated for the deposition of ruthenium, iridium and even osmium, though these are subject to limitations with regard to the thickness of sound coatings. Platinum metal coatings may also be produced from fused cyanide electrolytes⁵, a technique which is useful in those cases (e.g. ruthenium and iridium) where coatings of sufficient thickness cannot be produced from aqueous solutions. Iridium coatings of this type have been studied in connection with the high-temperature protection of molybdenum⁶, and thick coatings of rhodium have been produced in a similar way⁷. Since they are deposited at a temperature of the order of 600°C from a non-aqueous medium, such coatings tend to be less stressed, softer and less porous than coatings from aqueous solutions. For example, rhodium from a bath of this type shows a hardness of approximately 300 H_v compared with about 900 H_v from a conventional sulphate electrolyte.

Limitations imposed upon the thickness of coating obtainable from aqueous solutions due to internal stress have been overcome in several directions. Atkinson⁸ has reported the production of ductile, crack-free platinum coatings from a chloro-platinic acid plus hydrochloric acid electrolyte. Tripler, Beach and Faust⁹ have achieved improvement in the protective value of platinum coatings from a diamminodinitritoplatinum(II) electrolyte by the use of the periodic reverse (p.r.) current technique, which is also widely applied in gold plating. Patent claims have been made for the production of crack-free rhodium deposits from sulphate electrolytes modified by the addition of magnesium salts¹⁰ or of selenic acid¹¹. Highly ductile palladium coatings have been produced by Stevens in thicknesses up to 5 mm from a tetramminepalladium(II) bromide electrolyte¹².

Non-electrolytic plating processes of the displacement type and of the auto-catalytic type have also been described. In the former, a thin film of the noble metal is formed on a base metal substrate by chemical replacement. The reaction may cease when the substrate is completely covered, or, as in the processes described by Johnson¹³ for the platinum group metals, attack of the substrate may continue through an essentially porous top-coat, which may exfoliate on prolonged treatment. Such processes are of main utility for short-term protection purposes, e.g. retention of solderability of electronic components during storage. In auto-catalytic processes, further deposition of metal is catalysed by the initial layer of the coating itself. Processes of this type have been described for both gold¹⁴ and palladium^{15,16}.

Electrodeposited Coatings

Silver and gold (Chapter 6) Apart from their traditional decorative

applications, both silver and gold find important industrial use in various types of chemical processing equipment. In the electrical and electronics industries they are employed as plated coatings on contacts and as finishes on wave guides, hollow conductors for high-frequency currents, etc. Silver plating is particularly used in the latter application where its high electrical and thermal conductivity are required in addition to its protective value. The thickness of coating necessary for adequate protection depends on the conditions of service and the nature and condition of the basis metal to which the coating is applied. For electrical purposes for the protection of aluminium, steel and copper, DTD 919A specifies a minimum thickness of 0.007 5 mm (0.000 3 in) of silver, with a total thickness of undercoat (copper or nickel) plus silver of 0.038 mm (0.001 5 in) on aluminium parts and 0.020 mm (0.000 8 in) on steel. BS 2816:1957 *Electroplated Coatings of Silver for Engineering Purposes* is also relevant in this context.

Laister and Benham¹⁷ have shown that under more arduous conditions (immersion for 6 months in sea-water) a minimum thickness of 0.025 mm of silver is required to protect steel, even when the silver is itself further protected by a thin rhodium coating. In similar circumstances brass was completely protected by 0.012 5 mm of silver. The use of an undercoating deposit of intermediate electrode potential is generally desirable when precious metal coatings are applied to more reactive base metals, e.g. steel, zinc alloys and aluminium, since otherwise corrosion at discontinuities in the coating will be accelerated by the high e.m.f. of the couple formed between the coating and the basis metal. The thickness of undercoat may have to be increased substantially above the values indicated if the basis metal is affected by special defects such as porosity.

In view of its susceptibility to sulphide tarnishing, silver may itself require some measure of protection in many decorative and industrial applications. Chromate passivation processes are commonly employed, but as an alternative, thin coatings of gold, rhodium or palladium may be used.

Although usage of gold plating in industrial applications has long outstripped that in traditional decorative fields, it was not until 1968 that an appropriate British standard was issued to cover both spheres of application¹⁸. The high reflectivity of gold in the infra-red region accounts for its use on reflectors in infra-red drying equipment, for which purpose a coating of 0.005 mm gives excellent service on beryllium-copper. This order of thickness became general for electrical contacts in the electronics field, where the main area of industrial gold plating is to be found; but thinner coatings are now usual. The basis metals involved are most commonly copper or copper-base alloys, e.g. brass, nickel-silver, beryllium-copper and phosphor bronze, and coating thickness is dictated not only by environmental conditions but by the need for mechanical wear resistance in sliding and wiping contacts, in which context the softness of pure gold deposits from cyanide electrolytes is generally a disadvantage.

Numerous proprietary electrolytes have been developed for the production of harder and brighter deposits. These include acid, neutral and alkaline solutions and cyanide-free formulations and the coatings produced may be essentially pure, where maximum electrical conductivity is required, or alloyed with various amounts of other precious or base metals, e.g. silver, copper, nickel, cobalt, indium, to develop special physical characteristics.

The hardness of such coatings may reach a maximum of about 400 H_V as compared with approximately 50 H_V for a soft gold deposit. A series of corrosion studies in industrial and marine atmospheres by Baker¹⁹ has indicated that the protective value of hard gold coatings is comparable with that of the pure metal, and that a thickness of only 0.0025 mm gives good protection to copper base alloys during exposure for six months.

In view of the high cost of gold there is a continuing urge to reduce coating thickness in industrial applications to the bare minimum consistent with adequate service life. It is claimed for example that the thickness of gold on a wiping contact can be reduced by using an undercoating of silver, e.g. 0.0075 mm of silver plus 0.00025 mm of gold. In this case a special problem arises, particularly at elevated temperature, due to diffusion of silver outwards through the gold layer, with formation of a tarnish film at the surface. This can be prevented by interposing a thin deposit of palladium or rhodium between the gold and silver layers²⁰.

At gold thicknesses below 0.005 mm significant porosity is likely to be present, and a great deal of work was directed to the study of factors affecting the degree of porosity of gold coatings²¹⁻²⁴, and to possible means of reducing this, or at least minimising its practical effect. Reduction of porosity can be achieved by the use of copper or nickel under-coats and patents claimed that a coating of platinum only 0.38 μm thick would substantially reduce porosity and improve the high temperature stability of 0.0025 mm gold coatings on copper²⁵. The effect of corrosion through pores in thin gold coatings on copper- or silver-base substrates can be minimised by applying a thin coating of palladium or rhodium, since sulphide tarnish products do not spread on these metals²⁶, whereas they readily spread over gold to form large areas of high contact resistance. Gold coatings on sliding contacts are often lubricated, and it is claimed that pores in the coatings may be effectively sealed, with marked increase in service life, by incorporating a suitable corrosion inhibitor in the lubricating system²⁷.

The Platinum Metals (Chapter 6)

Rhodium Rhodium is the most important of the platinum group of metals as an electrodeposited coating for protective purposes as shown by the fact that it is the only metal of the group for which a DTD Process Specification exists (No. 931). Major fields of application are the protection of silver from tarnishing in both decorative and industrial spheres, and the finishing of metallic reflectors and electrical contacts (particularly sliding or wiping contacts subject to mechanical wear and concerned with the transmission of very small electrical signals, e.g. in radar, telecommunication, and allied equipment, where freedom of the contact surface from films is a critical requirement). The special properties of the electrodeposited coating on which these applications depend are its high reflectivity, virtual immunity from attack by corrosive environments, its consequently low and stable contact resistance, and its extremely high hardness (approximately 900 H_V). A disadvantage of the deposit, as produced from conventional acid sulphate or phosphate plus sulphate electrolytes, is a high internal tensile stress, which may give rise to cracking in deposits thicker than

0.0025 mm and which, as indicated earlier, places strict limitations on the usefulness of the coating for protection against severely corrosive liquid environments. The value of rhodium in resisting atmospheric corrosion in environments ranging from domestic to marine and tropical exposure has, however, been amply demonstrated by experience, and it appears probable that further developments in technology may lead to still wider application.

In view of the high cost, when tarnish resistance of the surface is the only requirement it is customary to use the thinnest possible coatings of rhodium (0.00025–0.0005 mm). Since rhodium deposits in this thickness range, like thin electrodeposits of other metals, show significant porosity, readily corroding metals, e.g. steel, zinc-base alloys, etc. must be provided with an undercoating deposit, usually of silver or nickel, which is sufficiently thick to provide a fairly high level of protection to the basis metal even before the final precious metal deposit is applied, and, in this way, to prevent accelerated electrochemical corrosion at pores in the rhodium deposit.

It is not possible to plate rhodium directly on to reactive metals of the type mentioned above, in view of the acid nature of the electrolyte, but copper and its alloys, e.g. nickel-silver, brass, phosphor-bronze, beryllium-copper, which are of special importance in the electrical contact field, may be plated directly. Even in this case, however, an undercoat is generally desirable.

Whether nickel or silver is selected for use as an undercoating is determined by a number of factors, relative resistance to particular corrosive environments being clearly of primary importance. Laister and Benham¹⁷ have discussed the respective merits of the two metals on the basis of corrosion tests in a number of environments. Generally speaking, silver is preferred when the composite coating is required to resist exposure to marine or other chloride-containing atmospheres, the potential difference between silver and rhodium in sea-water at 25°C being only 0.05 V²⁸. A nickel undercoat is better for sulphide atmospheres and for operation at elevated temperatures (up to 500°C). In this connection, it should be noted that rhodium itself will begin to oxidise at temperatures in the range 550–600°C.

Silver is often preferred as an undercoat for rhodium by reason of its high electrical conductivity. A further advantage of silver in the case of the thicker rhodium deposits (0.0025 mm) applied to electrical contacts for wear resistance is that the use of a relatively soft undercoat permits some stress relief of the rhodium deposit by plastic deformation of the under-layer, and hence reduces the tendency to cracking²⁹, with a corresponding improvement in protective value. Nickel, on the other hand, may be employed to provide a measure of mechanical support, and hence enhanced wear resistance, for a thin rhodium deposit. A nickel undercoating is so used on copper printed connectors, where the thickness of rhodium that may be applied from conventional electrolytes is limited by the tendency of the plating solution to attack the copper/laminate adhesive, and by the lifting effect of internal stress in the rhodium deposit.

A thickness of 0.00038 mm may be regarded as a good quality finish for general decorative and industrial use for tarnish protection at normal temperatures. For optimum tarnish resistance at temperatures up to 500°C,

0.00125 mm of rhodium on a nickel undercoat is recommended. In sliding contact applications, where the ability of the coating to withstand some degree of mechanical wear is almost as important as tarnish resistance, the order of thickness employed is 0.0025–0.005 mm and, in a few special circumstances, this may be increased to 0.0125 mm or more.

Palladium Although satisfactory palladium plating processes have existed for many years, the metal was slow to attain industrial significance as an electrodeposited coating, but then became of considerable interest as an alternative to rhodium or gold in the finishing of electrical contacts, especially in copper end connectors of printed circuits³⁰. Apart from its relatively low cost, palladium has special technical advantages in this type of application. It may be deposited from neutral or slightly alkaline non-cyanide electrolytes which virtually do not attack the copper-laminate adhesives, the deposit shows only a low tensile stress, and it may readily be soldered, whereas rhodium presents some difficulty in this respect. Palladium has good contact properties and, in the electrodeposited condition, has a hardness of 200–300 HV which, while considerably lower than that of rhodium, is higher than that of most gold deposits, and affords a useful degree of wear resistance. Thicknesses of 0.0025–0.005 mm are usual, and the comments made previously regarding the porosity of thin coatings and the importance of undercoatings are applicable here too.

In sliding electrical contact applications, palladium plating has been criticised on the basis of a tendency due to its catalytic activity to cause polymerisation of organic vapours from adjacent equipment with the formation of insulating films on the surface³¹. This effect is important in certain circumstances, but is not serious in many practical applications³².

Platinum Since the ready workability of platinum permits cladding of base metal with sound coatings which may be as thin as 0.0025 mm uses of the metal in the electrodeposited condition for corrosion protection are relatively few. As in the case of palladium, electrolytes for platinum plating have been available for many years but interest in the process was greatly increased, chiefly in connection with the plating of titanium for the preparation of inert anodes for electrolytic processes³³. Attempts to use bare titanium as an anode in aqueous solutions result in the formation of a resistive oxide coating on the metal which prevents the passage of useful currents below about 15 V applied potential. At this potential, complete breakdown of the film occurs, with the onset of catastrophic corrosion. The presence of a thin layer of platinum on the titanium surface permits the passage of high currents at voltages well below the critical value, and in this application the presence of discontinuities in the electrodeposited platinum coating does not affect performance, since the exposed basis metal is sealed by a protective anodic film. This composite material, with a coating of platinum up to 0.0025 mm thick, was adopted for many electrode applications in which platinum-clad base metals or graphite were previously used, e.g. in brine electrolysis, peroxide and per-salt production, electrodialysis, cathodic protection, etc.

Studies suggested that under certain conditions platinum would become mechanically detached from titanium anodes owing to attack of the substrate through pores in the coating. Anodes became available with a

mechanically-clad platinum coating, and alternative coatings, e.g. of platinum-iridium alloy or ruthenium oxide were developed.

Ruthenium, iridium and osmium The use of a fused cyanide electrolyte is the most effective means for the production of sound relatively thick coatings of ruthenium and iridium, but this type of process is unattractive and inconvenient for general purposes and does not therefore appear to have developed yet to a significant extent for industrial application. This is unfortunate, since these metals are the most refractory of the platinum group and in principle their properties might best be utilised in the form of coatings. However, several interesting improvements have been made in the development of aqueous electrolytes.

For ruthenium, electrolytes based on ruthenium sulphamate³⁴ or nitrosyl-sulphamate³⁵ have been described, but the most useful solutions currently available are based on the anionic complex^{36,37} $(\text{H}_2\text{O} \cdot \text{Cl}_4 \cdot \text{Ru} \cdot \text{N} \cdot \text{Ru} \cdot \text{Cl}_4 \cdot \text{OH}_2)^{3-}$. The latter solutions operate with relatively high cathode efficiency to furnish bright deposits up to a thickness of about 0.005 0 mm, which are similar in physical characteristics to electrodeposited rhodium and have shown promise in applications for which the latter more costly metal is commonly employed. Particularly interesting is the potential application of ruthenium as an alternative to gold or rhodium plating on the contact members of sealed-reed relay switches.

Iridium has been deposited from chloride-sulphamate³⁸ and from bromide electrolytes³⁹, but coating characteristics have not been fully evaluated. The bromide electrolytes were further developed by Tyrrell⁴⁰ for the deposition of a range of binary and some ternary alloys of the platinum metals, but, other than the platinum-iridium system, no commercial exploitation of these processes has yet been made.

Electrodeposition of osmium⁴¹ was reported from a strongly alkaline electrolyte based on an anionic complex formed by reaction between osmium tetroxide and sulphamic acid. Little is known concerning the general soundness of such coatings, but they appear to show excellent mechanical wear-resistance, since in comparative abrasion tests an osmium coating lost only one-quarter the thickness of a hard chromium deposit. Both iridium and osmium have very high melting points and high work functions, which suggest application in the coating of tungsten valve grids to suppress secondary electron emission, but in both cases application is likely to be restricted by the high cost and limited availability of the metals.

Other Coating Techniques

'Brush' plating⁴² is a variant of electrodeposition in which the electrolyte is held in a pad of cotton wool or other absorbent material and applied by wiping over the article to be plated. Though very old in principle, modern developments in equipment and applicational techniques render the method extremely useful in the case of precious metals in view of the possibility of localising the coating to selected areas. It is also useful in repair and salvage operations in the plating of electronic components.

Another method entails application of the coating by spraying, brushing

or silk-screen printing onto the surface a liquid composition containing organic salts of the metal in a suitable vehicle, which, on firing, decomposes to produce a metal film. This process has been used for many years to apply very thin coatings of gold and other precious metals to non-conductors for decorative purposes, and has served as a basis for technological improvement designed to make it possible to apply thick coatings of platinum in a single application⁴³. Though developed initially for the coating of refractories for critical applications in the glass industry, the process is useful also in the coating of metals carrying refractory oxide films, e.g. titanium, zirconium. It has the merit that the properties of the coating are sometimes closer to those of the pure metal than is generally the case for electrodeposits.

Protection at High Temperatures

Although the platinum metals have high melting points, covering a range from 1552°C (palladium) to approximately 2500°C (ruthenium and iridium) only platinum retains its freedom from oxide films at temperatures up to the melting point. Palladium and rhodium form stable protective oxide films over a temperature range of approximately 500–1000°C, above which the oxides dissociate. The oxides formed by ruthenium and osmium are readily volatile, hence these two metals are quite unsuitable for high temperature application. The behaviour of iridium in this respect is intermediate between that of rhodium and ruthenium.

At temperatures above the melting point of gold, which represents the chief range of interest, the life of a platinum coating on a base metal is limited by the extent to which inter-diffusion with the substrate metal, and gaseous diffusion through the outer coating (leading to formation of base metal oxide initially along grain boundaries of the coating and ultimately at the surface) is possible. The problems involved are exemplified in the application of platinum coatings for protecting molybdenum against oxidation at temperatures in the region of 1200°C in gas turbines, and in the preparation of clad-molybdenum stirrers for molten glass. Useful life of the composite material is obtained only with claddings 0.25–0.5 mm thick, and in this connection Rhys⁴⁴ has demonstrated the importance of an intermediate layer of gold or an inert refractory oxide as a barrier to outward diffusion of molybdenum⁴⁵.

Although electrodeposition permits the coating of relatively complex shapes, the permeability of coatings so applied to gases at temperatures of the order of 1200°C is, in the present stage of development, too great for them to have a protective value comparable to that of wrought metal coatings. For example, an electrodeposit of platinum 0.10 mm thick protected molybdenum for only 16 h in air at 1200°C, whereas a mechanical cladding of this thickness had a life of some 300 h under similar conditions. It is possible, however, that modified coatings might be more akin to the pure metal in this respect. Coatings produced by vapour-phase deposition may possibly have advantages in this type of application.

An interesting approach to the inter-diffusion problem was made by Rhys⁴⁶ who protected ruthenium-rich ruthenium-gold alloys by palladium-

gold coatings of composition corresponding to the opposite ends of the 'tie-lines' in the palladium–gold–ruthenium ternary system. Since substrate and coating compositions are in thermal equilibrium, diffusion between the two does not occur to an appreciable extent over long periods at high temperatures. Unfortunately, coating life is again limited by diffusion of oxygen through the coating.

Recent Developments

Electrodeposited Coatings

Silver and gold Silver is nearly always deposited from cyanide baths, though other baths have been described. To limit oxidation and polymerisation in high-speed selective plating with insoluble anodes, low-cyanide baths have been developed containing salts such as phosphate⁴⁷.

Silver coatings may blister above 200°C because of oxygen diffusion. A nickel undercoat stops interdiffusion with a copper substrate above 150°C. Alloying with antimony, selenium, sulphur or rhenium increases hardness—the coefficient of friction is also much reduced in the last case⁴⁸.

Clarke's study of the porosity of gold deposits lasted for a decade^{23,49}. Reviewing the topic, Garte concluded that, to reduce porosity: (1) the substrate surface should be smoothed chemically or electrochemically; (2) certain undercoats are beneficial; and (3) plating conditions must be tightly controlled⁵⁰. Better procedures led to a reduction of thickness requirements—e.g. from 5 to 2.5 µm on connectors, provided other requirements are satisfied.

Abbott studied the corrosion of contacts, and proposed quality tests in dilute mixtures of hydrogen sulphide, nitrogen dioxide and chlorine in air at controlled temperature and humidity⁵¹. These gave good results in a project seeking improved procedures for British and IEC standards⁵².

Hundreds of baths exist for electrodeposition of gold and its alloys⁵³. The latter are more wear resistant, so better for contacts⁵⁴. Polymers incorporated in cyanide-bath deposits affect wear and contact resistance⁵⁵.

The Platinum Metals

Rhodium Patents have been filed on low-stress deposits, better undercoats and use of soluble anodes; there have been several reviews⁵⁶, but no major recent developments.

Palladium Advantages have been claimed for new baths (e.g. using chelated complexes⁵⁷). Antler summarised the use of palladium as coatings, inlays and weldments in electronic connectors⁵⁸. Crosby noted that palladium deposits are of two kinds: (1) soft but continuous or (2) hard but porous or cracked. To resist wear and substrate corrosion on contacts, he proposed the application of type 1 (from a bath with tetranitropalladium(II) anion) over type 2 (from solution containing tetramminepalladium(II) cation)⁵⁹.

Industry, however, favours electrodeposited palladium–nickel alloy since it is cheaper than palladium, harder and less prone to cracking, finger-printing and formation of polymer films⁶⁰. Its wear resistance is poor, so it is usually given a thin topcoat of hard (sometimes, soft) gold⁶¹.

Palladium–silver alloy has greater resistance to fretting. Inlays are common, and coatings will be adopted as deposition processes improve⁶².

Platinum Platinum-coated titanium is the most important anode material for impressed-current cathodic protection in seawater. In electrolysis cells, platinum is attacked if the current waveform varies, if oxygen and chlorine are evolved simultaneously, or if some organic substances are present⁶³. Nevertheless, platinised titanium is employed in tinplate production in Japan⁶⁴. Although ruthenium dioxide is the most usual coating for dimensionally stable anodes, platinum/iridium, also deposited by thermal decomposition of a metallo-organic paint, is used in sodium chlorate manufacture⁶⁵. Platinum/ruthenium, applied by an immersion process, is recommended for the cathodes of membrane electrolysis cells⁶⁶.

Characteristics of established platinum plating baths have recently been reviewed⁶⁷. Advantages have been claimed for new baths based on the complex tetrammineplatinum(II) cation⁶⁸.

Ruthenium, iridium and osmium Baths based on the complex anion $(\text{NRu}_2\text{Cl}_8(\text{H}_2\text{O})_2)^{3-}$ are best for ruthenium electrodeposition⁶⁸. Being strongly acid, however, they attack the Ni–Fe or Co–Fe–V alloys used in reed switches. Reacting the complex with oxalic acid gives a solution from which ruthenium can be deposited at neutral pH. To maintain stability, it is necessary to operate the bath with an ion-selective membrane between the electrodes⁶⁹.

Iridium and osmium are rarely deposited. A new osmium bath is based on the hexachloroosmate ion⁷⁰. Procedures were outlined for depositing osmium on targets for nuclear reactions⁷¹.

Other Coating Techniques

The largest uses of platinum group metals in electronics are: ruthenium for resistors and palladium for multilayer capacitors, both applied by thick film techniques⁷². Most anodes for brine electrolysis are coated with mixed ruthenium and titanium oxide by thermal decomposition⁷³. Chemical vapour deposition of ruthenium was patented for use on cutting tools⁷⁴.

Protection at High Temperatures

The life of gas turbine blades is improved by platinum and/or rhodium, applied below or above, or co-deposited with, aluminised, thermal-barrier or MCrAlY-type layers⁷⁵. The performance of modified aluminides was demonstrated in long-term engine trials⁷⁶.

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14 PROTECTION BY PAINT COATINGS

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14.1 Paint Application Methods

Methods of applying paint today are numerous and it is impossible to list and describe them in detail in a section of this size. Where corrosion resistance of the finished article is a major consideration, it is possible to apply controls to ensure that maximum corrosion protection is obtained from the selected application process.

Application Methods

In any method of application, either an excess of paint is applied and the surplus is removed, or the desired thickness of paint is put on directly. For simplicity, methods can be divided into cycling and non-cycling processes, i.e. procedures which return surplus paint to the plant and those which do not.

Cycling Processes

For these processes, the paint must not only meet the specification and end requirements of the finished product, but it must also be stable over long periods under operating conditions. The simplest form of the cycling paint process is the standard dip tank which can vary from a simple hand dip in a container of paint, to a sophisticated mechanised system. In the conveyorised process, articles pass into the dip tank, are withdrawn at a controlled rate, and, after draining, are allowed to air dry or are cured in a stoving oven. In such a system a large volume of paint is involved with a large surface area exposed to atmosphere. The bulk paint is continuously contaminated by the excess paint draining from the articles and any extraneous substances introduced with the articles. These contaminants can be controlled by filtering and circulating the paint. Constant control of viscosity, and paint composition are necessary if uniform results are to be obtained and, in modern sophisticated plants, these factors are regulated continuously by automatic equipment.

Flow coating In this process, paint is directed on to the workpiece from a series of strategically placed jets in an enclosed area and the excess paint

drains back to the main supply tank. The workpieces are then allowed to drain in a solvent-saturated zone (to delay evaporation and permit paint flow) before passing on to a flash-off zone and final stoving. Articles are usually hung from a monorail and accurate jigging is essential.

Curtain coating With this process, paint falls in a continuous curtain from a closely machined gap in a header tank on to the flat article passing below on a horizontal conveyor; the excess paint is collected in the main tank and then passed up to the header tank. It is an ideal method of applying thicker coatings (60 μm and above) to sheet metalwork.

Electrodeposition This method of paint application is basically a dipping process¹. The paint is water-based and is either an emulsion or a stabilised dispersion. The solids of the paint are usually very low and the viscosity lower than that used in conventional dipping. The workpiece is made one electrode, usually the cathode, in a d.c. circuit and the anode can be either the tank itself or suitably sized electrodes sited to give optimum coating conditions. The current is applied for a few minutes and after withdrawal and draining the article is rinsed with de-ionised water to remove the thin layer of dipped paint. The deposited film is firmly adherent and contains a minimum of water and can be stoved without any flash-off period. This process is used for metal fabrications, notably car bodies. Complete coverage of inaccessible areas can be achieved and the corrosion resistance of the coating is excellent (Fig. 14.1).

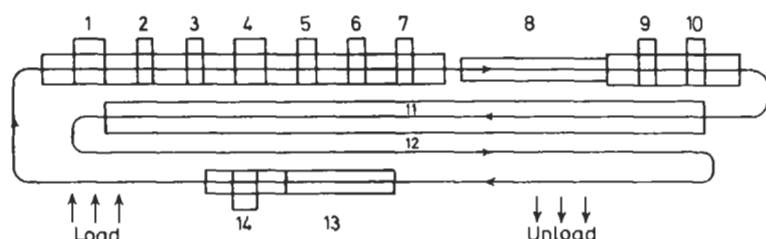


Fig. 14.1 Typical plant layout for electropainting (courtesy Stein, Atkinson Stordy Ltd.)

LEGEND

- | | |
|------------------------------|--|
| 1. Alkali degrease | 8. Paint dip |
| 2. Cold water rinse | 9. First rinse (town water) |
| 3. Hot water rinse | 10. Second rinse (demineralised water) |
| 4. Zinc phosphate | 11. Stoving oven |
| 5. } and | 12. Cooling leg |
| 6. } Cold water rinses | 13. Jig strip |
| 7. Demineralised water rinse | 14. Jig rinse |

Fluidised bed This process is used for powder coating². Basically, the equipment consists of a dip tank with a perforated shelf near the bottom. The powder is placed on this shelf and low pressure air is fed under the perforated shelf, resulting in a cloud of fine powder in the body of the dip tank. The article is heated to a little above the melting point of the powder and is then dipped into the fluidised bed for a short period. It is then withdrawn

and the coating cured in an oven. Thick films are formed, but it is difficult to obtain uniform film thickness with varying gauge metals.

Non-cycling Processes

These are processes in which the paint is used once only and the excess material is not returned to the main bulk. A typical example is the normal spray system in which the paint is fed to the spray gun, atomised by air jets and applied to the article as a stream of small droplets. The excess paint and overspray are deposited on the walls of the booth and are collected by various methods depending on the type of spray booth used³. There are many modifications of the conventional spray system which include the following.

Hot spray The paint is heated to 60–80°C. The hot paint flows better and gives better coverage. Transfer efficiency is increased and drying time is shortened.

Airless spray In this process, a high pressure (12–35 MN/m²) is applied to the paint to force it through a fine orifice in the spray gun. This process allows rapid transfer with reduced overspray.

Air assisted airless spray This concept is a combination of air spray and airless methods. Paint can be atomised with full spray patterns at low pressures. Turbulence is reduced significantly and overspray is minimised.

Electrostatic spraying This process takes advantage of electrostatic attraction. It is suitable for applying either liquid or powder coatings. Paint droplets or powder particles are passed through a powerful electrostatic field and become charged. They are attracted to the earthed workpiece and coat not only the front surface but also the back surface to a large extent if the object is not too deep or too wide. Automatic plant is available with spray guns on reciprocators.

Electrostatic hand guns The same principle has been adopted on portable hand guns. These modifications facilitate the coating of electrically shaded areas.

Brush Application of paint by brushing is still a commonly used method for maintenance painting. Coverage of large areas is slow and the quality of finish achieved relies heavily on the skill and motivation of the painter.

Paint Processes

Although the results obtained from a particular process depend almost entirely on the nature and design of the article, the plant layout and other local conditions play an important part. Table 14.1 gives some indications of the limitations of the processes mentioned.

Pressures to reduce atmospheric pollution, increase safety in the workplace, and save energy have all influenced paint application methods in

Table 14.1 Summary of process limitations

<i>Process</i>	<i>Uses</i>	<i>Limitations and defects</i>
Dipping	All types of articles of suitable shape and size	<ol style="list-style-type: none"> 1. Requires large throughput 2. Gives uneven film thickness on large flat sheets (from top to bottom) 3. Does not cover sharp edges or interior of channel sections, etc. 4. Possibility of solvent wash, i.e. solvent vapour from the hotter area condensing on cooler areas during flash-off and stoving
Flow coating	Suitable for use on most articles. Gives good penetration into pores of castings	Similar to dipping, but the defects not so marked. Tendency for greater solvent loss.
Curtain coating	Only suitable for flat sheets of uniform dimensions	On suitable articles this method will produce a uniform paint film providing the surface of the article is perfectly clean.
Electrodeposition	Suitable for most articles	Gives uniform film even on rough surfaces. With suitable plant will completely coat interior surfaces, sharp edges, etc. but generally only economic on mass production
Fluidised bed	Most suitable for small articles	Produces thick films. Varying metal gauge could produce uneven films and weak spots
Conventional spray	Suitable for most components	Very difficult to obtain adequate cover on inside corners, etc. and results depend on the skill of the operator
Airless spray	Suitable for most components	Superior penetration in awkward areas to normal spraying.
Electrostatic spraying (automatic)	With suitably designed plant, most articles can be painted with this process	Only economical in long runs. Very difficult to obtain adequate cover in electrically shaded areas and interiors of hollow articles
Brushing	Suitable for use on most articles, but use limited for economic reasons. Results rely almost entirely on skill of the operator	Labour cost is high

recent years. Emerging trends can be expected to continue and automation wherever possible, with increased use of water-thinned coatings and powder coatings, can be expected.

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14.2 Paint Formulation

Constituents of Paint

Paint consists essentially of a pigment dispersed in a solution of a binding medium. The binding medium or binder, which in most instances is organic, will decide the basic physical and chemical properties of the paint, but these will be modified by the nature and proportion of pigments present. In a decorative finish, for example the primary function of the pigment is to provide colour, but in a primer it should contribute to the durability of the whole system in a variety of ways depending on the substrate to which it is applied. The sole function of the volatile component or solvent is to control the viscosity of the paint for ease of manufacture and for subsequent application. Thereafter the solvent evaporates and is lost. A further class of paint is based on a binder emulsified in water. This type of paint has increased in importance in recent years and there is considerable evidence that good anticorrosive properties can be built into paints which themselves are thinned with water. The development of these paints is attracting considerable attention because of the absence of fire hazards, a low level of harmful vapours, and performance comparable with products carried in stronger solvents.

Since the possible variations in binder alone are limitless, it is possible to produce an infinite number of paints. As the range of raw materials available to the formulator becomes wider, their chemical purity is continually being improved. Mathematical models of binders can be constructed using computers and it is usually possible to predict fairly accurately the properties of a particular formulation before it is made. Nevertheless, the formulation of paints for specific purposes is still considered to be very much a technological art.

Although formulation is an art, science finds its place in the characterisation of the raw materials, in the design and testing of the series of experimental formulae and in the interpretation of the results. In addition to possessing an intimate knowledge of pigments, binders and solvents, the paint formulator must also be well acquainted with raw material costs and availability, paint making machinery, and the market's performance requirements.

Basic Principles of Formulation

Before any attempt is made to formulate a paint it is necessary to know a great deal about the conditions under which it will be used and subsequently

exposed. The more comprehensive the information relating to requirements, the greater the probability of achieving complete success with the first practical trial.

The conditions under which the paint will be dried, e.g. air drying or stoving, and the properties demanded in service will dictate the choice of binder. This, in turn, will limit the choice of solvents, and further constraints may be imposed by the presence of potential fire hazards at the user's works, or the problem of toxic fumes in enclosed working spaces. The quantity of solvent in the paint will depend on the intrinsic viscosity of the binder and the paint viscosity appropriate to the method of application, e.g. brushing, spraying, dipping, electrostatic spray, electrocoating, flow coating, etc.

A single paint will rarely possess all the required properties and it therefore becomes necessary to formulate a system comprising a primer, a finish, and possibly one or more intermediate coats.

A primer, as its name implies, is the first coat of a system. Its principal functions are to provide adhesion and good protection to the substrate. The manner in which these properties are obtained will vary with the substrate, but frequently involves the use of a large proportion of a specific pigment. This may impose a restriction on the colour and gloss, and probably on other desirable properties such as durability.

The finish or final coat must make up the deficiencies of the primer by affording it protection and providing the required colour and degree of gloss. These last two requirements will dictate the quality and quantity of the pigments to be used.

In the majority of cases maximum durability will be produced by a multi-coat system comprising priming and finishing paints only. Other considerations, however, such as uniformity of colour and smoothness of surface, may make it desirable to introduce intermediate coats, e.g. putty, filler and undercoat. The appearance of the final film or of the final painted structure is of some importance, and a final colour coat, which may contribute very little resistance to corrosion, may be necessary.

Putties are heavy-bodied pastes of high pigment content that are applied by knife for rough filling of deep indentations, more especially in rough castings.

Fillers are used to level-out shallower imperfections. Ease of flattening is an important consideration and to a large extent influences the composition and proportion of the pigment mixture.

Undercoats are invariably of high pigment content and low gloss. Their function is to provide a foundation that is uniform in both colour and texture for the finishing coats, thereby enhancing the final appearance of the completed system. On occasions, it is possible to achieve the same result by substituting an additional coat of finish for the undercoat, and this may improve the durability of the system.

When considering the number of coats of paint to achieve adequate protection it is worth noting that the cost of applying the paint usually far outweighs the cost of the paint. This is leading to a class of relatively more expensive paints which can be applied in very thick coats. The increasing mechanisation of painting methods, such as the airless spraying of structural areas, influences the paint formulator in the selection of the most suitable formulations.

However comprehensive the information relating to requirements, the paint technologist cannot proceed with the problem of formulating a suitable paint unless he is in possession of considerable data on the properties of the raw materials at his disposal, but within the scope of the present work it is impossible to do more than indicate the important properties of the more commonly used ingredients*.

Binding Media

The most important component in the majority of paints is the binding medium, which determines the physical and chemical properties of the paint. Blends of binding media are often used to impart specific properties to the dry paint film or to suit a particular application method. The compatibility of chemically different types of binders is an important factor to be taken into account by the paint formulator. These properties will be modified, however, to a greater or lesser extent by the nature and quantity of the other components, more especially the pigment. The general characteristics of various binding media are given in Table 14.2.

Drying Oils (treated and untreated)

Apart from being basic ingredients of oil varnishes and alkyd resins, drying oils are occasionally used as the binder in paint. Linseed oil is an important drying oil and is the only one used to any extent in its natural state. Its main use is in corrosion-inhibiting primers. Disadvantages of paints based on raw linseed oil are their very slow drying, lack of gloss, and inability to flow sufficiently for brushmarks to level out. The mechanism of the protective action of these primers is considered in Section 14.3.

Heat-treated oils fall into three categories: boiled oils, stand oils and blown oils. Boiled oils are prepared by heating linseed oil in the presence of catalysts. They have somewhat higher viscosities and better drying properties due to their higher molecular weights and more complex molecular structure than raw linseed oil. They are commonly used in oil-based primers and, in conjunction with oil varnishes, in undercoats. Stand oils range in viscosity up to about 20 N s/m² and are prepared by heat-polymerising linseed oil either alone or in admixture with tung oil. They are used mostly in combination with oil varnishes and alkyd resins to improve application properties and, when desirable, to increase the total oil: resin ratio.

Blown oils differ from stand oils in that they are partially oxidised in addition to being polymerised. The oxidation is achieved by blowing air through the heated oil. This treatment results in a product having poor drying properties, and blown oils are therefore effective plasticisers and are used as such in nitrocellulose finishes.

* A list of relevant standard texts is given at the end of this section, but the principal sources of detailed information are in the form of technical data sheets issued by raw-material suppliers.

Table 14.2 General characteristics of binding media

<i>Type of binder</i>	<i>Mode of drying</i>	<i>Solvents</i>	<i>Acid resistance</i>	<i>Alkali resistance</i>	<i>Water resistance</i>	<i>Solvent resistance</i>	<i>Exterior weathering resistance</i>	<i>Special features</i>
Raw linseed oil Boiled linseed oil Stand oils	Air drying Oxidative polymerisation	Aliphatic hydrocarbons	Fair	Bad	Fair	Poor	Poor/fair	Binder for anti- corrosive primers for wire-bushed steel Slow drying
Oleoresinous varnishes	Air drying and/or stoving Condensation and/or oxidative polymerisation	Aliphatic and/or aromatic hydrocarbons	Fair	Bad	Fair/good	Poor	Fair/good	Pale-coloured finishes that yellow on exposure
Long oil length alkyds	Air drying Oxidative polymerisation	Aliphatic hydrocarbons	Fair	Bad	Fair	Poor	Very good	
Medium oil length alkyds	Air drying and/or stoving Oxidative and/or condensation polymerisation	Aliphatic and aromatic hydrocarbons	Fair	Poor	Fairly good	Fair	Very good	
Short oil length alkyds	Stoving Condensation polymerisation	Aromatic hydrocarbons	Fair	Fair	Good	Fairly good	Very good	
Modified alkyds	Air drying and/or stoving Oxidative and/or	A wide range of solvents depending on	Fair	Fair	Usually good	Fair/	Usually good very good	

Table 14.2 (continued)

<i>Type of binder</i>	<i>Mode of drying</i>	<i>Solvents</i>	<i>Acid resistance</i>	<i>Alkali resistance</i>	<i>Water resistance</i>	<i>Solvent resistance</i>	<i>Exterior weathering resistance</i>	<i>Special features</i>
Urea formaldehyde /alkyd blends	Stoving Condensation polymerisation	Aromatic hydrocarbons and alcohols	Fairly good	Fairly good	Very good	Good	Fair	Water white Gives white finishes of excellent colour
Melamine formaldehyde/alkyd blends	Stoving Condensation polymerisation	Aromatic hydrocarbons	Fairly good	Fairly good	Very good	Good	Very good	Water white Gives white finishes of excellent colour
Epoxide/aliphatic amine or polyamide blends	Air drying Addition polymerisation	Blends rich in higher ketones	Fairly good	Very good	Poor	Very good	Fairly good/good	Finishes need to be supplied in two separate containers and mixed just prior to use
Epoxide/amino or phenolic resin blends	Stoving Addition and condensation polymerisation	Blends rich in higher ketones and alcohols	Good	Good	Very good	Very good	Good	
Epoxide/fatty acid esters	Air drying and/or stoving Oxidative polymerisation	Aliphatic and/or aromatic hydrocarbons	Fair	Fair	Fairly good	Poor	Poor/fairly good	
Polyester/polyisocyanate blends	Air drying or stoving Addition polymerisation	Blends rich in ketones and esters Alcohols excluded	Fairly good	Good	Fairly good	Very good	Very good	Finishes need to be supplied in two separate containers and mixed just prior to use

Table 14.2 (continued)

<i>Type of binder</i>	<i>Mode of drying</i>	<i>Solvents</i>	<i>Acid resistance</i>	<i>Alkali resistance</i>	<i>Water resistance</i>	<i>Solvent resistance</i>	<i>Exterior weathering resistance</i>	<i>Special features</i>
Vinyl resins	Air drying Solvent evaporation	Blends usually rich in ketones	Very good	Very good	Very good	Poor	Good	Fire hazard Flash point usually below 23°C
Chlorinated rubber	Air drying Solvent evaporation	Aromatic hydrocarbons	Good	Good	Very good	Poor	Good	Very poor heat resistance
Cellulose nitrate	Air drying Solvent evaporation	Blends of esters, alcohols and aromatic hydrocarbons	Fairly good	Bad	Good	Poor	Very good	Fire hazard Statutory regulations governing use

Oil Varnishes

The current practice is to classify as 'oil varnishes' all varnishes and paint media prepared from drying oils and natural or preformed oil-free synthetic resins. Examples of such resins are rosin, rosin-modified phenolics and oil-soluble 100% phenolics. The introduction of the resin results in improved drying and film properties.

Oil varnishes are capable of producing primers for ferrous metals which perform excellently on clean or pretreated surfaces, but they have not the same tolerance as their oil-based counterparts for wirebrushed rusted surfaces. The undercoats that follow are frequently also based on oil varnishes.

Since the individual members of this group of media differ considerably in properties, so also do the finishes that can be made from them. As a class, however, they are generally inferior to the better alkyds for durability under normal conditions. A particular exception is the tung-oil 100% phenolic type of medium, which produces finishes with very good resistance to water and mildly acidic or alkaline conditions; pale colours, however, discolour by 'yellowing' on exposure.

Alkyd Resins*

Introduced some 50 to 60 years ago, alkyd resins quickly established themselves and are still widely used. They are essentially polyesters of moderate molecular weight prepared by the reaction of polyhydric alcohols with the mixtures of monobasic fatty acids and dibasic acids. Ethylene glycol (dihydric), glycerol (trihydric) and pentaerythritol (tetrahydric) are the more commonly used alcohols. Phthalic anhydride is the most commonly used dibasic acid. Isophthalic acid and adipic acid are also used for special purposes. An unsaturated dibasic acid called maleic anhydride is widely used and can give polymers of high molecular weight. There is a very wide range of fatty acids available, the ultimate choice being dependent upon the properties required. The fatty acid is frequently added in the form of a vegetable oil which is a tri-ester of fatty acid and glycerol.

Individual alkyds are usually described in terms of the proportion and type of fatty acid and of the alcohol that they contain. Thus a 70% linseed-oil pentaerythritol alkyd would be expected to comprise linseed oil fatty acids, pentaerythritol and phthalic anhydride, with an equivalent of 70% linseed oil calculated on the weight of the non-volatile resin.

The members of this family are so diverse that only the fundamental properties can be considered here. For convenience they will be subdivided according to their use, i.e. (a) air-drying, (b) stoving, (c) plasticising and (d) modified alkyds.

Air-drying alkyd resins Alkyds capable of air drying do so through the oxidation of the drying oils that they contain. Such alkyds are consequently

*The synthesis of various types of resins is given in Section 14.9.

usually of long oil length*, i.e. 65 to 75% and based on the tetrahydric alcohol pentaerythritol. The oils most commonly used are linseed and soya bean. The latter imparts more freedom from yellowing to white- and pale-coloured finishes, especially where there is little natural light. Tung oil is less frequently used because it promotes yellowing. Sunflower oil, cottonseed oil, safflower oil and tall-oil fatty acids are being used more and more frequently for high quality white gloss paints. In some cases, the fatty acid is partly replaced by a synthetic organic monobasic acid which modifies the polymer solubility and film properties. Among the outstanding properties of air-drying alkyds are (a) their convenience in use and (b) their ability to give finishes of unrivalled durability in all but heavily polluted atmospheres. Where premature failure does occur, it probably results from poor surface preparation or an inadequate priming system.

Air-drying alkyds may also be used for the production of primers and undercoats. In the case of primers, the shorter the oil length of the binder the faster the drying, but the lower the tolerance for wire-brushed rusted-steel surfaces. Alkyd-based undercoats are not significantly different in performance from those based on oil varnishes; the choice is frequently dictated by economic considerations.

Stoving alkyd resins When drying is to be effected by stoving, the oxidative properties of drying oils are of less importance, and advantage can be taken of the tougher properties of the phthalic ester component of the resin. Hence stoving alkyds may be based on drying or semi-drying oils, and the oil length is invariably shorter than for air-drying finishes, usually in the range 50 to 65%.

For high-quality stoving finishes the alkyd is frequently blended with a lesser quantity of an amino resin. This reduces the stoving schedule and enhances most of the physical properties of the finish.

The inclusion of a small proportion of rosin during the manufacture of the alkyd will also improve application and initial film properties. Such binders are commonly used for stoving primers and for cheap stoving finishes that will not be subjected to exterior exposure.

Plasticising alkyd resins The term *plasticising* alkyd is a loosely used one, embracing those alkyds that are employed in conjunction with a larger proportion of another, and usually harder, stoving resin, e.g. an amino resin. In certain compositions the shorter-oil-length stoving alkyds referred to before may function as plasticisers, but in general plasticising alkyds are of even shorter oil length, usually 40 to 50%, and consist of fatty acids of non-drying oils, e.g. coconut oil.

* *Oil length* is the relative proportion of oil to resin in a binding medium. It is expressed in a variety of ways, including simple ratios and, as in the present text, the percentage oil calculated on the weight of the non-volatile binder. In the case of traditional varnishes it is a precise value calculated directly from the relative quantities of oil and resin used. With more complex binders, including alkyds, such simple calculations are not possible; various assumptions must be made and the values then obtained are essentially theoretical. The terms *long*, *medium*, and *short* oil length are used loosely to indicate respectively, high, medium and low proportions of oil. There are no generally agreed limits but in the present context *long* oil length is applied to binders containing more than 65% oil, *medium* oil length to binders having between 65 and 50% oil and *short* oil length to those containing less than 50% oil.

Modified alkyd resins In this group one finds styrenated alkyds, vinyl toluenated alkyds, oil-modified vinyl resins, acrylic alkyds, silicone alkyds and polyurethane alkyds. The modifying component usually has a number of effects. It always increases the molecular weight of the alkyd polymer, and may impart hardness, durability, or chemical resistance. It also affects the solubility of the polymer in solvents.

Amino Resins

The two amino resins in common use are urea formaldehyde and melamine formaldehyde, and most stoving finishes contain one or the other. They have many properties in common; urea formaldehyde, however, while substantially cheaper, has poor exterior durability, whereas melamine formaldehyde imparts excellent exterior durability. As they are both water white they give white finishes of excellent colour, with the additional advantage of retaining their colour on over-stoving. Urea formaldehyde is commonly used in conjunction with a lesser quantity of an alkyd to give finishes with excellent resistance to water and mild chemicals, which are therefore well suited to use on domestic equipment, e.g. washing machines.

Melamine formaldehyde is also used in conjunction with an alkyd, but the ratio varies considerably according to the ultimate use of the finish.

Epoxide Resins

Epoxide resins are essentially long-chain polyhydric alcohols with epoxide groups at either end. They make useful building blocks because both the hydroxyl and the epoxide groups are available for reaction with other compounds.

Aliphatic polyamines, amine adducts and polyamides react with epoxide resins at normal temperatures to give complexes with outstanding chemical resistance. Paints based on this type of reaction must be supplied in two separate containers, one containing the epoxide resin and the other the 'curing agent', the two being mixed in prescribed proportions immediately before use.

Amino resins and certain phenolics react with epoxide resins at elevated temperatures to give somewhat similar results. As the combination is non-reactive at normal temperatures this type can be supplied in the form of ready-for-use stoving finishes.

Epoxide resins can be esterified with fatty acids to give media ranging from air-drying to stoving types. The presence of fatty acid reduces the chemical resistance to the same order as that of the alkyds. It is nevertheless sometimes found advantageous to use an epoxy ester for certain specialised purposes.

Polyurethanes

Polyurethanes are essentially the reaction products of polyisocyanates and polyesters containing free hydroxyl groups. They are comparable with the

epoxide types in that they possess excellent chemical resistance but, by contrast, have very good colour and gloss retention. It is necessary to supply the air-curing types in two-pack containers. One-pack stoving types are formulated by using less reactive 'masked' isocyanates.

Another important group of products is the polyurethane oils and polyurethane alkyds. In these binders, the chemical linkages are a mixture of the highly chemically resistant urethane links and the less resistant ester links. It is very misleading and difficult to classify their properties because the ratio of urethane to ester linkages varies widely from one product to another. In many properties, they are very similar to alkyds, but usually possess more rapid drying, even at low temperatures, and give a slightly harder film initially. They are, however, less flexible than comparable alkyds and often slightly worse for exterior durability. The name *polyurethane* on a product cannot be taken as an indication of chemical resistance unless it is a two-pack polyurethane or a moisture-curing polyurethane.

Moisture-curable urethane systems (one-pack) can be considered as two-component systems which use atmospheric moisture as the second component. One-pack urethane coatings can be produced that are similar in physical properties to the two-pack systems for almost all applications. These highly complex systems can have a great deal of flexibility. Claimed advantages are: a one-pack system, rapid cure, even at low temperatures, excellent chemical and abrasion resistance and good flexibility. Although these systems have been available for some time in other countries of Europe, they are only recently beginning to be of interest in the UK.

Vinyl Resins

A wide range of resins prepared by polymerisation of compounds containing vinyl groups is available. Those most commonly used in paint manufacture are of the following types:

- (a) Essentially copolymers of vinyl chloride and vinyl acetate or vinyl ether.
- (b) Emulsified vinyl acetate copolymers.
- (c) Acrylic modified alkyds, etc.

A characteristic of the group (a) of resins is that they air-dry solely by solvent evaporation and remain permanently solvent soluble. This fact, combined with the need to use strong solvents, makes brush application very difficult, but sprayed coats can be applied at intervals of one hour. A full vinyl system such as (a) possesses excellent chemical and water resistance. Many members of group (a) have very poor adhesion to metal, and have therefore been exploited as strip lacquers for temporary protection. Excellent adhesion is, however, obtained by initial application of an etching primer; the best known of such primers comprises polyvinyl butyral, zinc tetroxy-chromate and phosphoric acid.

The chemical resistance of group (b), frequently used in emulsion or latex paints, is often upset by the presence of water-soluble emulsion stabilisers and thickeners, which remain water soluble in the dried paint film.

Group (c) has already been discussed under the heading *modified alkyds*.

Chlorinated Rubber

Chlorinated rubber is soluble in aromatic solvents, and paints made from it dry by solvent evaporation alone. In contrast to the vinyls, there is less difficulty in formulating systems that are suitable for brush application. It has excellent resistance to a wide range of chemicals and to water, but as it is extremely brittle it needs to be plasticised. To preserve chemical resistance it is necessary to use inert plasticisers such as chlorinated paraffin wax. Due to the presence of ozone depleting solvents, chlorinated rubber coatings are being phased out and largely replaced by vinyl acrylic coatings which have very similar performance and can be formulated from lower aromatic or aliphatic solvents.

Nitrocellulose

Paints containing nitrocellulose are of importance in relation to the protection of metals because of their excellent durability combined with very fast drying. They may, on this account, be used for mass-production work where stoving facilities are not available, and it is interesting to recall that had such paints not been available the mass production of motorcars would inevitably have been delayed. Their rapid drying makes them unsuitable for brush application to large areas, but a more serious disadvantage is the fire hazard associated with nitrocellulose, and users of such paints must comply with stringent statutory regulations.

Nitrocellulose alone will not give a continuous coating. It must, therefore, be blended with other components comprising a plasticiser and a hardening resin. An extensive range of such products is available, the ultimate choice depending on the properties required.

Miscellaneous Binders

These consist of the following:

- (a) Silicone polymers having high heat stability and excellent chemical resistance are available. They are very expensive and hence are not commonly found in paint coatings.
- (b) Silicate binders are used in conjunction with zinc powder to give paints of excellent corrosion resistance. The organo-silicates, e.g. ethyl orthosilicate, are most commonly used. The full potential of this type of binder has probably not yet been exploited.
- (c) Thixotropic binders.
- (d) Fluorinated polymers such as polytetrafluorethylene are available for specialised applications. Titanium polymers with excellent heat stability are available. New polymers are being developed all the time, especially by the plastics industry, and the aforementioned groups of binding media are merely those commonly used, and do not constitute a complete list. It may, however, illustrate the range of products

and properties available to the paint formulator for the selection of the most appropriate binders in the paint.

Pigments

In a finish, the function of the pigment is to provide colour, but in a primer it should contribute to the protection of the metal substrate and enhance the adhesion of the finishing system. Pigments are essentially dry powders which are insoluble in the paint medium and which consequently need to be mixed in it by a dispersion technique. They range from naturally occurring minerals to man-made organic compounds and may be subdivided broadly into priming pigments, colour pigments, extenders and metal powders.

Extenders are chemically inert, naturally occurring or synthetic, inorganic compounds which are included to confer specific properties to the paint. Such properties include suspending the pigment to prevent the formation of hard settlement, improvement of 'build', and the provision of 'tooth' or 'key' to improve intercoat adhesion.

Red lead, zinc chromate, calcium plumbate and zinc dust were for many years of special importance as pigments for metal primers. When dispersed in raw or lightly-treated linseed oil, the first three possess the ability to inhibit the corrosion of mild steel and will function very well on wire-brushed rusted surfaces. In other media the tolerance towards rusted surfaces decreases with decreasing quantities of available oil, but performance on clean steel will usually be maintained and often improved.

Zinc phosphate is now probably the most important pigment in anticorrosive paints. The selection of the correct binder for use with these pigments is very important and can dramatically affect their performance. Red lead is likely to accelerate the corrosion of non-ferrous metals, but calcium plumbate is unique in providing adhesion to newly galvanised surfaces in the absence of pretreatment, and is claimed to behave similarly on other metals in this group.

Primers containing 93–95% zinc dust by weight in non-saponifiable media provide sacrificial protection to clean steel (see Section 14.3).

Pigments for finishes are selected on the basis of their colour, but special attention must be paid to inertness in the chosen binder and stability and light fastness under the conditions of application and exposure. Flake pigments such as aluminium and micaceous iron oxide give finishes of lower moisture-vapour permeability than conventional pigments, and consequently contribute to better protection.

Paint Additives

A paint rarely consists solely of pigment dispersed in a solution of a binder. For one reason or another, small quantities of ancillary materials called *additives* are included. The oldest and still the most important are the 'driers' which are used in all air-drying and many stoving paints containing drying oils. They are organic salts of certain metals, notably cobalt, calcium, barium, zirconium and manganese, with lead very much in decline.

Anti-oxidants are of value in preventing skinning in containers, but care must be taken to ensure that they do not adversely affect the drying properties of the paint. They are also used to reduce the oxidation of the excess paint that drains from dip-coated articles back into the dip tank.

Surface-active agents are used to facilitate the dispersion of pigments, to keep the pigment in suspension during storage of the paint, and to preserve the homogeneity of pigment mixtures while a paint is drying.

Another group of additives are used as thickeners and antisettle agents. They affect flow and reduce sagging of thick films.

Solvents

The term *solvent* is loosely applied to the volatile component of a paint, though this component may in fact consist of a true solvent for the medium plus a non-solvent or diluent. When such a mixture is used, usually with the aim of reducing cost or obtaining a higher solids content at a given viscosity, care must be taken to ensure that the diluent is more volatile than the true solvent in order that the medium shall remain in solution during the drying process.

A small amount of a particular solvent may be needed to aid application, to enable the release of small air bubbles in sprayed films, or to activate thickeners.

Classification of solvents is normally by chemical composition, e.g. aliphatic or aromatic hydrocarbons, alcohols, esters, ketones, etc. In addition to knowing which are appropriate for use with particular media, the paint formulator must also be acquainted with the fire hazards associated with the individual solvents and mixtures thereof, and the toxicity of various mixtures. Regulations governing Occupational Exposure Limits and ventilation requirements play an important role in the choice of solvents in a coating composition. There are both statutory and transport regulations relating to the use and carriage of paints, according to their 'flash point' and the composition of their solvent.

Paint-making Machinery

For the purpose of paint formulation the most important units of equipment are the laboratory ball mill, bead mills and high speed dispersers. The most common, the ball mill, consists of a cylindrical porcelain vessel a little more than half filled with steel, porcelain balls or pebbles. Pigment, together with sufficient binder and solvent to make a free-flowing mix, is loaded into the mill until it is approximately two-thirds full. The mill is then closed and fixed into a device whereby it is made to rotate about its major axis. Normally, a period of about 16 hours is required for thorough dispersion of the pigment, whereupon the mill-base is emptied out and blended with the remainder of the ingredients.

The selection of the appropriate type of machinery and the determination of the optimum conditions for bulk manufacture is usually the subject of discussion between the paint formulator and a senior member of the

production department. For most pigment/resin bases there will usually be more than one milling machine suitable for producing the required degree of dispersion. Different types of dispersion equipment can be classified on the basis of milling action, and by considering how pigment agglomerates are broken up. All mills operate by crushing or shearing or both together, and each one will work best within fairly close limits of mill-base viscosity. Machines working mainly by crushing require a low mill-base viscosity and those relying on shearing need a high one.

In principle, the selection of dispersion equipment for a given purpose is very simple. The obvious choice is the one that will give the required degree of dispersion most economically. In practice it is not so easy. Availability of equipment, the nature of the raw materials, mill-base formulation, batch size, product type and the time available all influence the decision of which machine to use.

Formulating a Paint

The paint technologist entrusted with the task of formulating a paint to meet a specified set of conditions must first decide what type of binders he should use and the type of solvent blend that this will require. In the particular case of a finish, he must then select the pigments most likely to give the required colour, bearing in mind any limitations imposed by his choice of binder system or by the conditions to which the paint will be subjected.

With the aid of a palette knife, weighed quantities of the several pigments are ground by hand into a binder such as linseed oil until an approximate match to the colour pattern is obtained. The consistency of this paste can be adjusted instrumentally to obtain the maximum work from the particular dispersion unit to be used. On the basis of this rough estimate, a premix is prepared with the appropriate quantities of pigment, binder and solvent, and a high-pigment-content mill-base is produced. From this and subsequent mill-bases, ordered series of paint samples are prepared and tested to establish the following data:

- (a) The most appropriate pigment: binder ratio.
- (b) In the case of a composite binder system, the optimum proportion of each.
- (c) The optimum addition of additives, e.g. driers, that may be necessary.
- (d) The appropriate viscosity and solvent composition.

If, as is possible, the first mill-base gives a poor colour match, the relative proportions of the several pigments are suitably adjusted in subsequent experiments. The ultimate aim should be to obtain a colour that is slightly deficient in the stronger tinting strength pigments, since it is more convenient to produce an exact match to the pattern by making small additions of high tinting strength mill-bases than by making larger additions of weaker bases.

Assuming that a paint with satisfactory properties has now been produced, there remains the possibility that it may deteriorate on storage. This must be investigated, and any faults that develop must be corrected.

The ability to apply knowledge gained by practical experience is the hallmark of a good paint formulator, for it frequently enables him to proceed to an acceptable basic formulation without delay. The greater part of the limited time that he has been allowed can then be devoted to perfecting his product. It is worthy of note, however, that the development of new products for exterior exposure is inevitably a slow process because there is no accelerated weathering cycle that can be relied upon to reproduce faithfully the effects of natural weathering.

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14.3 The Mechanism of the Protective Action of Paints

From time to time astronomical estimates are made of the annual destruction of metals, particularly iron and steel, by corrosion (Section 1.1). Paint is one of the oldest methods used for delaying this process and consequently it is somewhat surprising that its protective action has only recently been systematically examined.

Since iron is the commonest structural material, the following discussion will be limited to the behaviour of this metal. The general principles can readily be extended to non-ferrous metals.

The Corrosion of Iron and Steel (Sections 1.4 and 3.1)

Corrosion is essentially the conversion of iron into a hydrated form of iron oxide, i.e. rust. The driving force of the reaction is the tendency of iron to combine with oxygen.

It has long been known that iron is not visibly corroded in the absence of either water or oxygen. The overall reaction in their presence may be written:

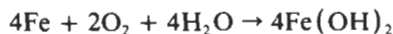


When the supply of oxygen is restricted the corrosion product may contain ferrous ions.

The overall reaction can be broken down into two reactions, one producing electrons and the other consuming them:



or



In the presence of oxygen the ferrous hydroxide will be converted into rust, $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

Ferrous hydroxide is soluble (9%) in pure water, but slight oxidation renders it appreciably less soluble. Thus in the presence of water and oxygen alone the corrosion product may be formed in close contact with the metal and attack will consequently be stifled. In the presence of an electrolyte such

as sodium chloride, however, the anodic and cathodic reactions are modified, ferrous chloride being formed at the anode and sodium hydroxide at the cathode. These two compounds are very soluble and not easily oxidised, so that they diffuse away from the sites of formation and react at a distance from the metal surface to form ferrous hydroxide, or a basic salt, which then combines with oxygen to form rust, with the regeneration of sodium chloride:



Consequently rust is formed at a distance from the metal and stifling cannot occur.

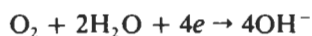
It follows that when iron rusts, the conversion is accompanied by a flow of electrons in the metal from the anodic to the cathodic regions, and by the movement of ions in solution. This conclusion has been firmly established by Evans¹ and his co-workers, who have shown that, in the case of a number of metals under laboratory conditions, the spatial separation of the anodic and cathodic zones on the surface of the metal was so complete that the current flowing was equivalent to the corrosion rate (see Section 1.6).

In order to inhibit corrosion, it is necessary to stop the flow of current. This can be achieved by suppressing either the cathodic or the anodic reaction, or by inserting a high resistance in the electrolytic path of the corrosion current. These three methods of suppression are called *cathodic*, *anodic* and *resistance* inhibition respectively (Section 1.4).

The effect of paint films on the cathodic and anodic reactions will now be considered and the factors which influence the electrolytic resistance of paint films will be discussed.

The Cathodic Reaction

The cathodic reaction in neutral solutions usually involves oxygen, water and electrons:



If a paint film is to prevent this reaction, it must be impervious to electrons, otherwise the cathodic reaction is merely transferred from the surface of the metal to the surface of the film. Organic polymer films do not contain free electrons, except in the special case of pigmentation with metallic pigments; consequently it will be assumed that the conductivity of paint films is entirely ionic. In addition, the films must be impervious to either water or oxygen, so that they prevent either from reaching the surface of the metal.

The rate of corrosion of unpainted mild steel immersed in sea-water was found by Hudson and Banfield² to be 0.089 mm/y. Hudson³ obtained a similar average value for steel exposed in the open air under industrial conditions (0.051 mm/y at Motherwell and 0.109 mm/y at Sheffield). This rate of corrosion corresponds to the destruction of 0.07 g/cm² per year of iron. Assuming that the corrosion product was Fe₂O₃·H₂O, this rate of

attack represents the consumption of 0.011 g/cm^2 per year of water and 0.03 g/cm^2 per year of oxygen.

Diffusion of Water

The diffusion of water through paint films has been measured by various workers. The weight of water which could diffuse through three clear vehicles and eight paint films, each 0.1 mm thick, at 85–100% r.h. has been calculated on the assumption that the water would be consumed as soon as it reached the metal surface, i.e. that the rate-controlling step was the rate of diffusion of water through the film, and is shown in Table 14.3^{4,5}.

Table 14.3 Diffusion of water through paint films of thickness 0.1 mm

<i>Vehicle</i>	<i>Pigment</i>	<i>Rate of water consumed ($\text{g cm}^{-2} \text{y}^{-1}$)</i>	<i>Reference</i>
Glycerol phthalate varnish	None	0.825	4
Phenolformaldehyde varnish	None	0.718	4
Epoxy coal tar	None	0.391	5
Glycerol phthalate varnish	Flake aluminium	0.200	4
Phenolformaldehyde varnish	Flake aluminium	0.191	4
Linseed oil	Lithopone	1.125	4
Ester gum varnish	White lead/ zinc oxide	1.122	4
Linseed penta-alkyd	Iron oxide 15% p.v.c.	0.840	5
Linseed penta-alkyd	Iron oxide 35% p.v.c.	0.752	5
Epoxy polyamide	Iron oxide 35% p.v.c.	1.810	5
Chlorinated rubber	Iron oxide 35% p.v.c.	1.272	5

Note. Unpainted steel consumes water at a rate of $0.008\text{--}0.023 \text{ g cm}^{-2} \text{y}^{-1}$

By means of an ingenious instrument which measured the 'wetness' of a painted surface, Gay⁶ found that although the relative humidity of the atmosphere varies appreciably, this is not reflected in the behaviour of paint films. He found that under normal conditions paint films are saturated with water for about half their life, and for the remainder the water content corresponded with an atmosphere of high humidity; furthermore, the relative humidity of sea-water is about 98%. It follows from Table 14.3 that the rate at which water passes through paint and varnish films is many times greater than the water consumed by an unpainted specimen exposed under industrial conditions or immersed in the sea.

Diffusion of Oxygen

The diffusion of oxygen through polymer films has been examined by a number of workers. Guruviah⁵ measured the permeability to oxygen of films cast from five paints (Table 14.4) and compared the results with the

corrosion rates of painted steel panels, when exposed to salt spray and humidity for 1 000 h. He concluded that 'the low corrosion rate could be explained by the low permeability to oxygen of the films'; however, when his values for the permeability are plotted against the corrosion it is clear that this conclusion is without foundation.

The weight of oxygen which could diffuse through unit area of a 0.1 mm thick film under a pressure gradient of 2 kN/m² of oxygen has been calculated, and is shown in Table 14.4^{5,7,8}. Baumann¹⁹ has claimed that these figures are about 100 times too high, but this is because he compared the amount which could pass through in a day with that passing in a year. Haagen and Funke⁵⁵ concluded that the permeation of water was too great and that of ions too small to be the controlling factor and suggested that the rate controlling step was the rate of the diffusion of oxygen. However, if this were the case then painted steel upon exposure should corrode at a rate varying from that of unpainted steel to about a tenth of that value. Since painted steel upon exposure does not corrode immediately at this rate, it is concluded that the rate of the diffusion of oxygen is not the controlling factor.

Table 14.4 Diffusion of oxygen through paint films of thickness 0.1 mm

<i>Vehicle</i>	<i>Pigment</i>	<i>Rate of oxygen consumption (g cm⁻² y⁻¹)</i>	<i>Reference</i>
Asphalt	None	0.053	7
Epoxy coal tar	None	0.002	5
Polystyrene	None	0.013	8
Polyvinyl butyral	None	0.027	8
Asphalt	Talc	0.039	7
Linseed penta-alkyd	Iron oxide	0.003	5
	15% p.v.c.		
Linseed penta-alkyd	Iron oxide	0.003	5
	35% p.v.c.		
Epoxy polyamide	Iron oxide	0.002	5
	35% p.v.c.		
Chlorinated rubber	iron oxide	0.006	5
	35% p.v.c.		

Note. Unpainted steel consumes oxygen at a rate of 0.020–0.030 g cm⁻² y⁻¹

The general conclusion drawn from these considerations is that paint films are so permeable to water and oxygen that they cannot inhibit corrosion by preventing water and oxygen from reaching the surface of the metal, that is to say they cannot inhibit the cathodic reaction.

The Anodic Reaction

The anodic reaction consists of the passage of iron ions from the metallic lattice into solution, with the liberation of electrons, which are consumed at the cathode by reaction with water and oxygen.

There are two ways in which the anodic reaction can be suppressed:

- (a) If the electrode potential of iron is made sufficiently negative, positively charged iron ions will not be able to leave the metallic lattice, i.e. cathodic protection.
- (b) If the surface of the iron becomes covered with a film impervious to iron ions, then the passage of iron ions into solution will be prevented, i.e. anodic passivation.

Cathodic Protection (Chapter 10)

In order to make the potential of iron more negative, the iron must receive a continuous supply of electrons. As has already been pointed out, polymer films do not contain free electrons; there remains the possibility of obtaining these from a pigment. The only pigments which contain free electrons are metallic ones, and such pigments will protect iron cathodically if the following conditions are fulfilled:

- (a) The metallic pigment must be of a metal less noble than iron, otherwise the iron will supply electrons to the pigment, which will be protected at the expense of the iron.
- (b) The pigment particles must be in metallic, i.e. electronic, contact with each other and with the coated iron; if they are not the movement of electrons cannot occur.

It has been shown⁹ that zinc dust is the only commercially available pigment which fulfils both conditions. Paints capable of protecting steel cathodically can be prepared with zinc dust, provided that the pigment content of the dried film is of the order of 95% by weight; both organic and inorganic binders have been used, the latter being very useful when resistance to oil or organic solvents is required.

These paints are quite porous and function satisfactorily only in the presence of an electrolyte—e.g. water containing a trace of salt, or acid—which completes the circuit formed by the two metals. It might be thought that the useful life of these paints is limited to the life of the electronic contact between the zinc particles, but this is not correct. Under normal conditions of exposure the electrons supplied by the zinc to the steel are consumed at the surface of the steel by reaction with water and oxygen (cathodic reaction), with the formation of hydroxyl ions. Consequently the surface becomes coated with a deposit of the hydroxides, or carbonates, of zinc, calcium, or magnesium, which blocks the pores in the film and renders it very compact, adherent and impervious. Thus, although metallic contact between the steel and the zinc dust particles is essential in the *early* stages of exposure, the paints provide good protection after that contact has been lost. Paints containing less zinc dust have been known for a long time, but as the zinc dust concentration is decreased, protection at scratch lines or at gaps in the coating, decreases; however, such paints frequently afford good general protection owing to the formation of deposits (consisting of oxides and carbonates) on the metal at the base of the coating.

Recently it has been pointed out that manganese satisfies both conditions, since the oxide film around the particles contains ions in two states of oxidation, and it has been claimed that cathodically protective paints can be

prepared with this pigment¹⁰. Exposure trials in this country have indicated that at an inland site their behaviour is comparable with the zinc dust controls, but that they were inferior to zinc-rich paints under severe marine conditions. It has been suggested that they might be of interest where zinc was unsuitable owing to toxicity¹¹.

Anodic Passivation (Section 10.8)

When a piece of iron is exposed to the air, it becomes covered with an oxide film. Upon immersion in water or solutions of certain electrolytes, the air-formed film breaks down and corrosion ensues. In order to prevent corrosion the air-formed film must be reinforced with similar material, or a ferric compound, and there are two ways in which this may be achieved:

- (a) The pigment may be sufficiently basic to form soaps when ground in linseed oil; in the presence of water and oxygen these soaps may autoxidise to form soluble inhibitive degradation products.
- (b) The pigment itself may be an inhibitor of limited solubility.

Basic pigments Typical pigments in this class are basic lead carbonate, basic lead sulphate, red lead and zinc oxide.

It has been established that water becomes non-corrosive after contact with paints prepared by grinding basic pigments in linseed oil¹²; it was also shown that lead and zinc linoleates, prepared by heating the oxide with linseed oil fatty acids in xylene, behave in a similar way. Later this observation was extended to the linoleates of calcium, barium and strontium¹³.

Determinations have been made of the solubility of lead linoleate prepared in the absence of oxygen and extracted with air-free water¹⁴. Under these conditions, lead linoleate had a solubility of 0.002% at 25°C and the extract was corrosive when exposed to the air. When, however, the extraction was carried out in the presence of air, the resulting extract contained 0.07% solid material and was non-corrosive. It was concluded that in the presence of water and oxygen lead linoleate yielded soluble inhibitive degradation products.

In order to obtain information regarding the composition of these degradation products, aqueous extracts of the lead soaps of the linseed oil fatty acids were analysed, mainly by chromatography. The extracts contained formic acid 46%, azelaic acid 9% and pelargonic acid and its derivatives 27%, the remaining 18% consisting of a mixture of acetic, propionic, butyric, suberic, pimelic and adipic acids. It was shown that whereas the salts of formic acid were corrosive, those of azelaic and pelargonic acid were very efficient inhibitors.

Ramshaw¹⁵ has obtained information regarding the origin of these various acids by examining the degradation products of the lead soaps of the individual acids present in linseed oil. He found that it was only the unsaturated acids which degraded to give inhibitive materials, and that the lead soaps of linoleic and linolenic acid yielded in addition short-chain acids which were corrosive. He also examined the relative inhibiting powers of the lead, calcium and sodium salts of a range of mono- and di-basic acids

in the pH range 4–6 at concentrations of 10^{-3} to 10^{-5} N¹⁶. Under these conditions the lead salts were always more efficient than the sodium and calcium salts, and the optimum efficiency occurred when both the mono- and di-basic acids had a chain length of 8–9 carbon atoms.

The mechanism of inhibition by the salts of the long chain fatty acids has been examined¹⁷. It was concluded that, in the case of the lead salts, metallic lead was first deposited at certain points and that at these points oxygen reduction proceeded more easily, consequently the current density was kept sufficiently high to maintain ferric film formation; in addition, any hydrogen peroxide present may assist in keeping the iron ions in the oxide film in the ferric condition, consequently the air-formed film is thickened until it becomes impervious to iron ions. The zinc, calcium and sodium salts are not as efficient inhibitors as the lead salts and recent work has indicated that inhibition is due to the formation of ferric azelate, which repairs weak spots in the air-formed film. This conclusion has been confirmed by the use of ¹⁴C labelled azelaic acid, which was found to be distributed over the surface of the mild steel in a very heterogeneous manner¹⁸.

Zinc phosphate was introduced as an inhibitive pigment by Barraclough and Harrison⁵⁶, and in the early tests vehicles based on drying oils were used. Later it was claimed⁵⁷ that it was an effective inhibitive pigment when used with all paint media in current use.

Variable results have been reported with this pigment and an examination of its inhibitive action⁵⁸ has led to the conclusion that under rural and marine conditions, where the pH of the rain-water is above 5, it behaves as an inert pigment owing to its limited solubility. However, in industrial and urban areas, where the pH of the rain-water may be in the region of 4 or lower, it is converted into the more soluble monohydrogen phosphate. This reacts in the presence of oxygen, with the steel surface to form a mixture of tribasic zinc and ferric phosphates, which being insoluble protects the steel from further attack.

Soluble pigments The most important pigments in this class are the metallic chromates, which range in solubilities from 17.0 to 0.00005 g/l CrO_3 ⁽²⁰⁾. An examination has recently been carried out of the mechanism of inhibition by chromate ions and it has been shown by chemical analysis of the stripped film, Mössbauer spectroscopy and electron microprobe analysis that the air-formed film is reinforced with a more protective material in the form of a chromium-containing spinel²¹ (Chapter 17). The situation is, however, complicated by the possibility that some chromates, particularly the basic ones, may inhibit through the formation of soaps. There is evidence that lead chromate can function in this way.

It has been found that red lead, litharge and certain grades of metallic lead powder render water alkaline and inhibitive¹²; this observation has been confirmed by Pryor²². The effect is probably due to a lead compound, e.g. lead hydroxide, in solution. Since, however, atmospheric carbon dioxide converts these lead compounds into insoluble basic lead carbonate, thereby removing the inhibitive materials from solution, these pigments may have only limited inhibitive properties in the absence of soap formation.

Work by Beckmann²³ indicated that lead hydroxide was only very slightly better as an inhibitor than sodium hydroxide, and the mechanism

of inhibition is probably similar to that suggested for alkaline solutions²⁴.

Owing to the low dielectric constant of organic vehicles, these pigments can ionise only after water has permeated the film, consequently their efficiency is associated with the nature of the vehicle in which they are dispersed, a point which is sometimes overlooked when comparing the relative merits of chromate pigments.

Resistance Inhibition

It has been shown that paint films are so permeable to water and oxygen that they cannot affect the cathodic reaction, and that the anodic reaction may be modified by certain pigments. There are, however, many types of protective paint which do not contain inhibitive pigments. It is concluded that this class of paint prevents corrosion by virtue of its high ionic resistance, which impedes the movement of ions and thereby reduces the corrosion current to a very small value.

It is assumed that conduction in polymer films is ionic — it is difficult to see how it could be otherwise — and the factors which break down this resistance, or render it ineffective, will now be considered.

The effective resistance of paint films may be influenced by ions derived from three sources:

- (a) Electrolytes underneath the film.
- (b) Ionogenic groups in the film substance.
- (c) Water and electrolytes outside the film, i.e. arising from the conditions of exposure.

Electrolytes Underneath the Film

Atmospheric exposure trials, carried out in Cambridge, established the fact that when rusty specimens were painted in the summer, their condition, after some years' exposure, was very much better than that of similar specimens painted in the winter²⁵. It was found that steel weathered in Cambridge carried spots of ferrous sulphate, deeply imbedded in the rust, and that the quantity of ferrous sulphate/unit area was very much greater in the winter than in the summer²⁶; this seasonal variation was attributed to the increased sulphur dioxide pollution of the atmosphere in the winter, caused by the combustion of coal in open grates. It was concluded that there was a causal relationship between the quantity of ferrous sulphate and the effective life of the paint. It was suggested that these soluble deposits of ferrous sulphate short-circuit the resistance of the paint film and, since paint films are very permeable to water and oxygen, the ferrous sulphate will become oxidised and hydrolysed with the production of voluminous rust, which will rupture the film at numerous points, thus giving rise to the characteristic type of failure seen on painted rusty surfaces.

It can be claimed that the problem of painting rusty surfaces is now understood. A method for estimating the ferrous sulphate content of any rusty surface has been put forward²⁶, but the amount of ferrous sulphate

which can be tolerated by various paints has not yet been established. Thus it is bad practice to apply paints to surfaces carrying electrolytes.

Ionogenic Groups in the Film Substance

Ionogenic (ion-producing) materials may be present, in the form of electrolytes, in both the pigments and the vehicle. Their presence in the pigments may be eliminated by the selection of suitable raw materials by the paint manufacturer, consequently it does not concern us here, but it is of importance to consider the possibility of the existence of ionogenic groups, such as carboxyl groups, in the polymer itself.

When paint films are immersed in water or solutions of electrolytes they acquire a charge. The existence of this charge is based on the following evidence. In a junction between two solutions of potassium chloride, 0.1 N and 0.01 N, there will be no diffusion potential, because the transport numbers of both the K^+ and the Cl^- ions are almost 0.5. If the solutions are separated by a membrane equally permeable to both ions, there will still be no diffusion potential, but if the membrane is more permeable to one ion than to the other a diffusion potential will arise; it can be calculated from the Nernst equation that when the membrane is permeable to only one ion, the potential will have the value of 56 mV.

It is easy to measure the potential of this system and it has been found²⁷ that membranes of polystyrene, linseed oil and a tung oil varnish yielded diffusion potentials of 43–53 mV, the dilute solution being always positive to the concentrated. Similar results have been obtained with films of nitrocellulose²⁸, cellulose acetate²⁹, alkyd resin and polyvinyl chloride³⁰.

This selective permeability is ascribed to the presence on the membrane of a negative charge, which is attributed to carboxyl groups attached to the polymer chains. Paint films can, therefore, be regarded as very large anions.

It has been shown³¹ that the charge influences the distribution of the primary corrosion products, and recent work has indicated that the existence of carboxyl groups in the polymer film has an important influence on its behaviour when immersed in potassium chloride solutions.

Water and Electrolytes outside the Film

Here we are concerned with the effect of ions in the environment on the resistance of polymer films.

Kittelberger and Elm³² measured the rate of diffusion of sodium chloride through a number of paint films. Calculations based on their results²⁷ showed clearly that the rate of diffusion of ions was very much smaller than the rate of diffusion of either water or oxygen. Furthermore, they found that there was a linear relationship between the rate of diffusion and the reciprocal of the resistance of the film. This relationship suggests that the sodium chloride diffused through the membrane as ions and not as ion pairs, since the diffusion through the film of un-ionised material would not affect the resistance, because if a current is to flow, either ions of similar charge

must move in one direction, or ions of opposite charge must move in opposite directions.

An examination has, therefore, been made of the effect of solutions of potassium chloride on the electrolytic resistance of films cast from a pentaerythritol alkyd, a phenolformaldehyde tung oil and an epoxypolyamide varnish^{33,34}. Potassium chloride was chosen because its conductivity is well known and unpigmented films were first examined in order to eliminate the complexities of polymer/pigment interaction.

The experimental procedure consisted of casting the varnish on glass plates by means of a spreader bar having an 0.102 mm (0.004 in) gap; this produced a wet film 0.051 mm (0.002 in) thick that yielded a dried film of 0.025 mm (0.001 in). This standard thickness was used throughout and resistances are quoted in $\Omega \text{ cm}^2$. The cast films were dried for 48 h in a glove box followed by a further 48 h in an oven at 65°C.

The films were then soaked in water and removed from the plates. Portions were mounted in glass cells which were filled with potassium chloride solution; two Ag/AgCl electrodes were inserted into the limbs of the cells and the unit was placed in a thermostat. The resistance of the films was determined, from time to time, by connecting the cells in series with a known resistance and applying a potential of 1 V to the combination; the potential drop across the standard resistance was measured by means of a valve potentiometer.

When samples of about 1 cm² were taken from a single cast film of 100 × 200 mm of a number of paint and varnish films, their resistances varied with the concentration of potassium chloride solution in one of two ways (Fig. 14.2). Either the resistance increased with increasing concentration of the electrolyte (inverse or *I* conduction) or the resistance of the film followed that of the solution in which it was immersed (direct or *D* conduction). The percentage of *I* and *D* samples taken from different castings varied, but average values for a number of castings were 50% *D* for the pentaerythritol alkyd and the tung oil phenol formaldehyde varnishes, 57% for urethane alkyd, 76% for epoxypolyamide and 78% for polyurethane varnishes⁵⁰.

The effect of iron oxide, zinc oxide and red lead on the percentage of *D* areas has been determined. Three vehicles were used, a pentaerythritol alkyd, a tung oil phenolic and an epoxypolyamide⁴⁹. In the case of iron oxide, the *D* areas increased with all three vehicles; in contrast zinc oxide had very little effect on the percentage *D* areas. However, red lead when dispersed in the alkyd and tung oil vehicles behaved in a similar way to iron oxide, whereas red lead when dispersed in the epoxypolyamide vehicle had very little effect.

A careful examination has been made of the properties of *I* films when immersed in solutions of electrolytes. It was found that when a film of a pentaerythritol alkyd varnish was transferred from 0.001 N KCl to 3.5 N KCl its resistance rose, fell upon returning it to the 0.001 N KCl, rose again to the same high value when immersed in a sucrose solution isotonic with 3.5 N KCl and fell to the original value when returned to the dilute KCl solution (Fig. 14.3). It was concluded that the changes in resistance were dependent only upon the available water in the solution and were associated, therefore, with the entry of only water into the varnish film³³.

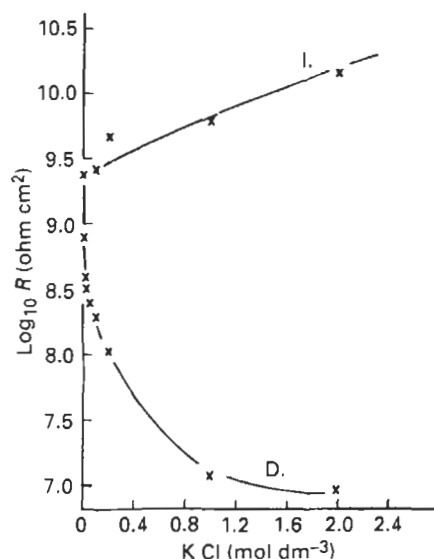


Fig. 14.2 Relationship between the logarithm of the resistance of *D* and *I* films of a pentaerythritol alkyd paint, containing 6.1% iron oxide by volume, and the concentration of the potassium chloride solutions in which they were immersed (courtesy *Brit. Polym. J.*, 3, 41 (1971))

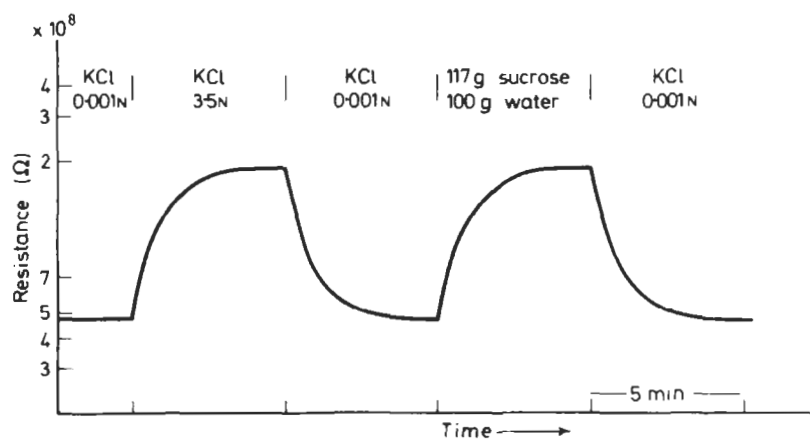


Fig. 14.3 Relationship between the resistance of an *I* film (log scale) and the concentration of the solute (courtesy *Official Digest*, 34 No. 452, 972-990, Sept. (1970))

In contrast, *D* films followed the resistance of the solution in which they were immersed, and this behaviour was originally explained by assuming that *D* films contained holes, or pores, filled with solution that controlled the resistance of the film. Thus a typical value for the resistance of a *D* film in 3.5N potassium chloride is $10^8 \Omega \text{ cm}^2$ and if this resistance was due to a pore, then it would have a radius of about 500 Å. In order to test this

explanation the distribution of *I* and *D* areas in a given piece of film has been determined by means of a series of gaskets fitted into a dismountable cell³⁶. It was found that *I* films were free from *D* areas, but that in the case of the three vehicles examined, samples of *D* films always contained a mixture of *I* and *D* areas in an interlocking mosaic structure. It was concluded that those portions of the film having *D* properties were distributed over an appreciable area of the sample and not confined to a single area, as would have been the case had the sample contained a single pore. It was concluded that *D* conduction cannot be attributed to the presence of pores, unless they were of molecular dimensions.

In general, the water uptake of *D* films tended to be higher than that of *I* films, but a more significant difference was shown by microhardness measurements. The results obtained with all three vehicles showed that the *D* areas were significantly softer than the *I* areas and that the distribution of the hardness values corresponded to that of the resistances. It was concluded that these films have a very heterogeneous structure and that *I* and *D* areas are brought about by differences in crosslinking density within the film.

An investigation has been made of the factors which control *I* and *D* conduction and it has been found that the difference is only one of degree and not of kind³⁵. Thus, if the varnish films are exposed to solutions of decreasing water activity, then the resistance falls with increasing concentration of electrolyte, but a point is eventually reached when the type of conduction changes and the films exhibit *I*-type behaviour. It appears that *D* films can be converted into *I* films, the controlling factor being the uptake of water.

The discussion so far has been limited to the behaviour of polymer films after immersion in potassium chloride solutions for only a short time. When varnish films were immersed in potassium chloride solutions for a month or more a steady fall in resistance took place. Further experiments indicated that the effect was reversible and dependent on both the pH of the solution and the concentration of potassium chloride. It was concluded that an ion exchange process was operative³³.

In view of this, the properties of *I* films were examined after they had been subjected to increasing amounts of ion exchange³⁴. In order to do this, detached films were exposed at 65°C for 7 h to a universal buffer adjusted to a suitable pH and the resistance of the film measured at 25°C in 3 N and 0.001 N potassium chloride. The results obtained with a pentaerythritol alkyd are shown in Fig. 14.4 from which it can be seen that as the pH of the conditioning solution increased, the resistance of the film fell, until at a pH of about 7.5 it suddenly dropped. The resistance of the film then followed that of the solution in which it was immersed, i.e. it became a *D*-type film. Similar results were obtained with films of a tung oil phenolic varnish, although in this case the change-over point occurred at a higher pH, i.e. about 9.

In the case of the epoxypolyamide varnish, however, as the pH increased the resistance of the film at first rose, then at about pH 8.8 it started to fall until at pH 11 the change-over in the type of conduction occurred. This suggests that the resin was acting as a zwitterion with an isoelectric point at about pH 8.8. Thus before the isoelectric point the membrane would be positively charged and an increasing concentration of hydroxyl ions would

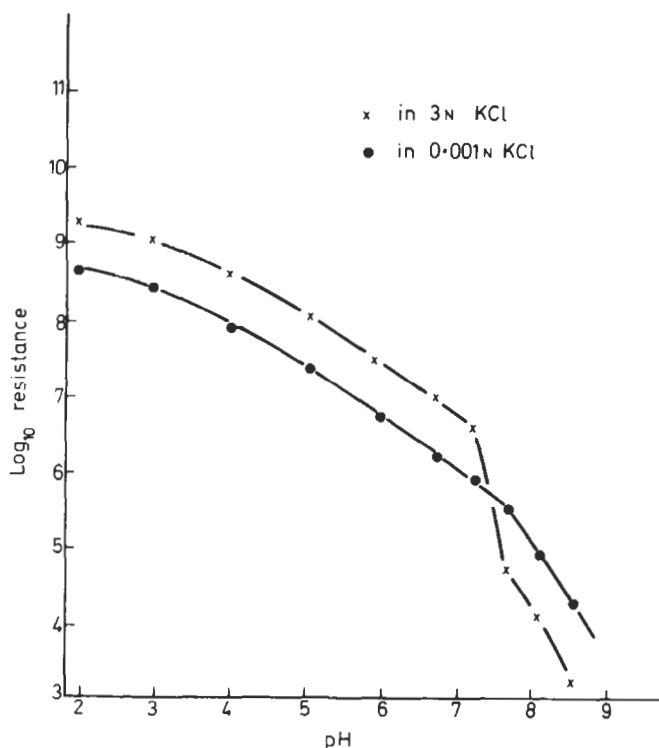


Fig. 14.4 Variation of the resistance of *I* films (log scale) with the pH of the conditioning solutions

depress the ionisation of the ionogenic groups; above the isoelectric point the membrane would be negatively charged and ion exchange with potassium ions would take place. This conclusion was confirmed by diffusion potential measurements.

In the case of all three varnishes after ion exchange had taken place, a point was reached when the type of conduction changed from *I* to *D*. The change-over in the type of conduction was found to occur at the same pH as a fall in the temperature coefficient of resistance, and the lower value corresponded to that of the aqueous solution.

The phenomenon of ion exchange has been confirmed by chemical analysis³⁷. Films were exposed to potassium chloride solutions of increasing pH, ashed and their potassium content determined by flame photometry. It was found that the potassium content of the films increased as the pH of the solutions rose until saturation was reached at a value which corresponded to that of the change-over in the mechanism of conduction. It was concluded that the change-over in the mechanism of conduction corresponded to the point at which the exchange capacity of the film had reached its limit.

Rothwell³⁸ found by resistance measurements that ion exchange occurred in films of eight unpigmented varnishes, and he confirmed this for penta-

erythritol alkyd films by the determination of the uptake of radioactive potassium in the form of ^{42}KCl ; however, his films, with one exception, were all *D* type.

Fialkiewicz and Szandorowski³⁹ examined the penetration of ^{90}Sr and ^{36}Cl ions through air-dried films of a styrenated alkyd pigmented with iron oxide over the range 10–60% p.v.c. (pigment volume concentration) and found intense penetration of the strontium cations, but negligible penetration of the chloride ions.

Ulfvarson *et al.*⁴⁰ examined the ion exchange properties of free films of a soya alkyd, and later Khullar and Ulfvarson⁴¹ extended the examination to clear films of 20 vehicles. They concluded that those binders with low ion exchange capacities provided the best protection. In a later study⁴² they examined the relationship between ion exchange capacity and corrosion protection of 22 paints based on three alkyd binders and concluded that ion exchange was not the dominating factor, but a secondary one. This conclusion was confirmed by van der Heyden⁴³, who suggested that a process of ion exchange combined with the diffusion of cations into the film was operative.

Physical Factors Affecting Resistance

The influence of temperature, the concentration of the electrolyte, film thickness and solvent on the resistance of paint and varnish films is discussed below.

Temperature An examination has been made of the effect of temperature on the structural changes in polymer films produced from the three vehicles described earlier⁴⁴. Three methods were used: dilatometry, water absorption and ionic resistance.

It was concluded that dilatometry was the most reliable method and water absorption is difficult to determine. Both methods use appreciable quantities of film, which contain both *D* and *I* areas. Resistance measurements, however, can be carried out on small areas of film and the relative properties of *D* and *I* areas studied.

It was established that significant changes in resistance took place at the transition temperature and consequently sharp changes in protective properties. The resistance always fell with an increase in temperature and this may provide an explanation for the fact that accelerated tests using the same corrosion cycle, may not produce the same results if carried out at different temperatures.

Concentration of Electrolyte Myer and Sievers⁴⁵ applied the Donnan equilibrium to charged membranes and developed a quantitative theory of membrane selectivity. They expressed this selectivity in terms of a selectivity constant, which they defined as the concentration of fixed ions attached to the polymer network. They determined the selectivity constant of a number of membranes by the measurement of diffusion potentials. Nasini *et al.*⁴⁶ and Kumins⁴⁷ extended the measurements to paint and varnish films.

When the Donnan equilibrium is operative the entry of ions into the membrane is restricted. Consequently as the concentration of ions in the solution increases the resistance of the membrane remains constant until the concentration of ions in the solution reaches that of the fixed ions attached to the polymer network. At this point their effect will be swamped and the movement of ions will be controlled by the concentration gradient.

Films of a pentaerythritol alkyd, a tung oil phenolic and an epoxypolyamide pigmented with iron oxide in the range 5–7% p.v.c. were exposed to solutions of potassium chloride in the range 0.0001–2.0 M⁴⁸. It was found that in all cases the resistance of the films steadily decreased as the concentration of the electrolyte increased. Since the resistances of the films were at no time independent of the concentration of the electrolyte, it was concluded that the Donnan equilibrium was not operative and that the resistance of the films were controlled by the penetration of electrolyte moving under a concentration gradient.

Film Thickness Varnishes prepared from the three standard polymers were cast at two thicknesses and the percentage of *D* areas compared with that obtained from films produced by casting one thin coat, allowing it to dry and then casting a second coat on top⁵⁰. Similar results were obtained from all three varnishes and the results obtained with the epoxylyamide varnish are given below.

	Thickness of coating (μm)	% <i>D</i> Type
Single coat	35–40	80
Single coat	75–80	50
Double coat	70–75	0–5

Earlier it was shown that *D* type areas are small; consequently the chance of *D* areas overlapping each other is low. It follows that two coats of all three varnishes, which are based on crosslinking polymers, are more effective in improving the resistance of the films than single coats of equal thickness.

Solvents All the films discussed so far have been cast from paints or varnishes containing solvents.

In order to examine the effect of solvents, films of a solvent-free epoxy-polyamine were cast, mounted in cells and their resistances measured in dilute and concentrated potassium chloride solution⁵¹. All the films had *I* properties with resistances in the range 10^{10} – $10^{12} \Omega \text{cm}^2$.

It appears that during the drying of paint or varnish films the presence of solvent molecules interferes with the process of cross-linking; consequently the films have a heterogeneous structure and films of improved protective quality arise when solvents are eliminated.

It is suggested that future work should be directed towards the pigmentation of solvent-free systems, either with inert pigments, when they would form coatings of high electrolytic resistance which would protect by the exclusion of ions, or as sealing coats applied over primers containing inhibitive pigments.

Prediction of Performance

If protection by paints or varnish films is due to their ability to restrict the penetration of corrosive ions, then it follows that resistance measurements should form the basis of the prediction of their behaviour. In 1948 Bacon *et al.*⁵² measured the resistance of over 300 paint systems immersed in seawater using a d.c. technique, and concluded that for good performance coatings should have a resistance in excess of $10^8 \Omega \text{ cm}^2$. Coatings having resistances in the range 10^6 – $10^8 \Omega \text{ cm}^2$ were found to be unreliable, and those of lower resistance behaved poorly.

It has frequently been suggested that during d.c. measurements the specimens become polarised, consequently a.c. current should be used. A comparison of d.c. and a.c. methods has been made and it was found that at a frequency of 1 592 Hz, and over the range 0.2–20 kHz the values of the resistances were always lower when a.c. was used⁵³.

The situation has now been clarified⁵⁴, and it has been shown that, with a.c., the values obtained are controlled by the capacitance until the frequency has fallen to about 1 Hz. It was shown that under these circumstances, in the absence of corrosion, the resistances of paint films measured by d.c. or a.c. were the same; furthermore, no polarisation resistance was detected.

The conclusions are that when coatings have resistances greater than $10^8 \Omega \text{ cm}^2$ (i.e. when corrosion is absent) then their resistances may be measured by either d.c. or a.c. However d.c. measurements can be made more quickly, they are easier to make and the apparatus is less costly. It has also been suggested that such measurements provide a basis for the prediction of performance. On the other hand, when corrosion has started, then a.c. should be used, since the values obtained can be resolved into two components, which provide a means of detecting and following the corrosion beneath the coating.

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14.4 Paint Failure*

In view of the wide scope of the subject, paint failure can be treated here only in general terms; detailed accounts will be found in the literature¹⁻⁶.

Forms of Paint Failure

A frequent defect of paintwork is cracking in all its forms, including checking, crazing and alligating, followed by such effects as flaking, scaling and peeling. These defects expose the underlying metal surface to the environment so that corrosion is not prevented. It should be observed that checking and crazing begin in the upper coat and extend gradually down towards the substrate, the fissures being wider on top and narrower towards the base. If such signs of breakdown become noticeable after a coating system has had a reasonable length of life in relation to the given conditions of exposure, it is not proper to consider them as film defects. Paint films start their gradual decomposition due to oxidation, erosion, weathering, etc. from the moment of exposure onwards at a rate dependent on their constituents, the environmental conditions and circumstances of application. With increasing age the elasticity of the film usually decreases (in the case of an oil-based or modified paint this results, in the main, from continued oxidation). Expansion and contraction of the metal base caused by severe temperature changes will result in the formation of discontinuities in a relatively inelastic paint film unless the paint has been formulated to withstand these conditions. Excessively high temperatures cause unsuitable paint films to become brittle, crack and lose adhesion. Loss of adhesion can also be caused by swelling.

Penetration of rust through an otherwise intact paint film is usually a result of inadequate surface preparation before painting, especially over weathered and hand-cleaned steel⁷. However, superficial rust staining may be traceable to dissolved iron salts, e.g. in bilge water from a ship's deck.

Causes of Paint Failure

A consideration of the most important causes of paint failure must include the following: inadequate surface preparation, application of the paint

* A glossary of the terms frequently used in this field will be found in Section 14.10.

under unfavourable conditions or by inappropriate methods, use of unsuitable paints, adhesion difficulties, the nature of the corrosive environment, etc.^{8†}.

Premature failure can also occur as a result of lack of attention to design. Facilities should, therefore, be provided for ventilatory drainage of water (rain, condensation, etc.), and all structures should be designed so as to permit ready access for repainting. Due consideration by architects and structural engineers at the design stage can indeed help to obviate certain of the causes of paint failure mentioned in this section (see also Sections 9.3 and 11.5).

Pretreatment and Paint Failure

The majority of failures of paint applied to metal surfaces are undoubtedly due to insufficient or unsatisfactory preparation of the metal surface, and it is essential that residues of dirt, grease, oil, silicone compounds, etc. be removed from the metal and that all loose paint be removed from surfaces which have been painted previously. The most common cause of premature failure is omitting to remove (as far as is practicable) corrosion products, e.g. rust and millscale, before painting. If a metal has been adequately pretreated, it is then desirable to apply the primer immediately at the factory, if this is possible, in order to ensure that the metal surface remains free from contamination and corrosion products. This is particularly important after grit blasting or any mechanical operations where a protective air-formed film may have been disrupted so that the metal is sensitive to corrosion. The condition of shop-applied primers should be examined before further painting, e.g. on site, and defective areas made good. Edges, welds and rivets need special attention. Pre-painted structural steel should not be left exposed unduly long to the weather, particularly under damp conditions or in a marine or industrial atmosphere, and should be handled carefully.

Priming

The first coat of paint applied to a surface has the major responsibility for establishing adhesion and for preventing corrosion. Hard-drying primers applied over loose millscale can result in wholesale stripping of scale and paint. Traditionally, oil-based red-lead primers were used over weathered and wire-brushed steel but it is safest to remove all the scale before priming. Etch primers, incorporating phosphoric acid to etch and clean the surface, substantially increase adhesion to metals that have not had a chemical pretreatment. Pretreatment with organo-functional silanes or incorporation of these materials in epoxy and polyurethane primers has been shown to improve adhesion to simply degreased steel and aluminium to levels approaching those on grit-blasted surfaces^{11,12}. Corrosion-inhibiting pig-

† Photographic standards are in use for the identification of the state of rusting at steel surfaces and of the quality of preparation before painting⁹; they distinguish between manual scraping and blast cleaning. Other photographic standards are used to classify the degree of rusting of painted steel¹⁰.

ments and their effectiveness in preventing underfilm corrosion are discussed in Section 14.3.

Effects of Climatic Conditions on Paint Films

Paint failure is related to climatic conditions, and the weather prevailing during application of the paint and during subsequent exposure will determine the life of the paint system. This applies, of course, particularly to outdoor work. In unfavourable weather conditions, cracking and blistering can be promoted as a consequence of the expansion of the products of corrosion, and in the case of iron and steel this can lead to under-rusting.

Low Temperatures and Wet Weather

When severe drops in temperature occur, outdoor work should if possible be halted, as hail, hoar frost and freezing conditions at the time of painting or shortly afterwards will greatly reduce the life of any paint film, as well as being detrimental to its appearance. Temperatures below 7°C, particularly in still, damp conditions during or immediately after application will prolong the drying time and may leave the film tacky for a long time. During this period dirt will adhere to the tacky film and rain or condensed moisture will tend to reduce the gloss by displacement of some of the paint.

Moisture-curing polyurethane paints and bituminous paints, specially formulated for the purpose, are also suited for application to damp substrates; other polyurethane paints should not even be applied to dry surfaces if the relative humidity is high.

Suitable paints for use underwater include vinyl resin systems, coal tar paints over inorganic zinc-rich primers, and some coal-tar epoxy primers have also proved themselves¹³. Special paints are available for application under water, e.g. epoxy modifications with polyamides.

Loss of matter by weathering induces hazing and loss of gloss, which are followed by chalking, usually a white film due to increased light scattering by loose pigment particles, but black on tar or bitumen. The chalking caused by the presence of titanium dioxide (especially anatase) in the top coat initiates rapid erosion. As the pigments in such defective films become more exposed to rain and wind and wash away, the films become increasingly permeable to moisture, with consequent corrosion of the underlying metal although they have the advantage of looking clean. In special cases (see below) controlled chalking may be desirable.

Painted metal exposed at coastal areas, ports and docks often suffers most from such hazards, which may be aggravated by high levels of u.v. radiation and the erosive action of blowing sand. Such conditions can prevail up to approximately 3 km inland.

Stripping of top coats soaked by rain or sea-water has occurred with alkyd-resin-based paint systems, mainly on ships. The risk of such inter-coat failure is reduced if the time interval between application of coats is reduced, but is best controlled by modification of the alkyd resin with a proportion of a different material.

Factors which can contribute to unsatisfactory drying, in particular of paints containing drying oils, include application of too-heavy paint films (especially during cold weather when viscosities and relative humidities are higher), overdoses of driers, gaseous pollution, use of unsuitable heavy thinners and residues of tar oil, wax or grease present on metal surfaces. Curing reactions of paints based on epoxy and polyurethane resins are markedly temperature dependent becoming extremely slow at temperatures below 5°C unless special hardeners are used; such paints should never be used below the minimum temperature specified by the supplier.

Tropical Conditions

Tropical conditions in general contribute to faster paint breakdown, owing to high temperatures, moisture-laden atmosphere, high ultra-violet content in the solar radiation, or to a combination of some or all of these effects. Thus in the tropical regions, fading and discoloration, matting, chalking and cracking, followed by peeling and general embrittlement, can take place rapidly. Chlorinated rubber paints fail especially in dry tropical environments, probably due to autocatalysed dehydrochlorination, whilst alkyd resin paints chalk more rapidly in wet tropical environments than in temperature conditions because of the greater amount of short wavelength u.v. radiation.

Effect of Industrial Atmospheres

In towns which are not heavily industrialised, the life of a paint film may be about equal to that in rural areas, but, because of traffic disturbance, dirt collection from soot and dust will be noticeable earlier. The use of self-cleaning (chalking) paints can overcome the premature loss of some of the decorative effect without noticeably reducing protection.

Industrial towns, especially those having heavy or chemical industries, have an acid atmosphere and the pH of rain water is sometimes as low as 3, owing to the presence of sulphuric acid. This can cause gradual attack on certain pigments and extenders, resulting in discoloration (e.g. red lead can be transformed into white lead sulphate, and atmospheric hydrogen sulphide results in the blackening of lead pigments) and decomposition of the paint film, and can lead to premature failure. Aluminium finishing paints applied over, for example, a red lead primer, are liable to be attacked in industrial atmospheres, owing to the formation of water-soluble aluminium salts, and the aluminium colour may disappear quickly. Similarly, top coats of zinc-rich paints may lose their metallic colour by formation of zinc salts (e.g. on iron chimney stacks), and contamination in the atmosphere may also endanger intercoat adhesion.

Effects of Moisture

Hot steam and severe condensation acting on a film surface exert a very destructive effect, comparable with that of a paint remover; they are particularly liable to cause swelling. Dry steam, in contrast to condensed steam, does not cause corrosion¹⁴. Less severe attack by water vapour can cause blistering, which can be of two types: intercoat blisters between paint films, and blisters through the complete film system. Only the latter leads to corrosion of the underlying material.

Paint films exposed to condensation often fail unexpectedly by very early blistering between primer and finishing coat, usually associated with soluble salts trapped under the relatively impermeable finishing coat. Relatively more permeable latex-based paints are less prone to this failure.

Dampness often accounts for the promotion of mould growth on painted surfaces, e.g. in breweries, laundries and dairies; fungi develop faster under tropical conditions. There are special media which are resistant to mould growth, in particular those which are based on the chlorinated compounds, such as chlorinated rubber, polyvinyl chloride, its various copolymers and other halogen-containing polymers. By addition of suitable fungicides and careful selection of the pigments, traditional hard-drying paints and varnishes can also be made to resist mould growth. Infected surfaces and films should be washed with fungicidal solutions before painting, but unless the source of infection is removed the trouble is likely to recur.

Factors Which Cause Paint Failure in Industrial Applications

Anti-oxidising Environments

Where fumes or deposits which act as anti-oxidants are present, no orthodox paint which dries by oxidation can give satisfactory service. Instead, a coating which dries either by evaporation (e.g. a selected chlorinated rubber paint), or by a cross-linking reaction (e.g. a catalysed epoxy or two-component polyurethane paint) must be used.

Oxidising and Acid Environments

Atmospheres polluted by oxidising agents, e.g. ozone, chlorine, peroxide, etc. whose great destructive power is in direct proportion to the temperature, are also encountered. Sulphuric acid, formed by sulphur dioxide pollution, will accelerate the breakdown of paint, particularly oil-based films. Paint media resistant both to acids, depending on concentration and temperature, and oxidation include those containing bitumen, acrylic resins, chlorinated or cyclised rubber, epoxy and polyurethane/coal tar combinations, phenolic resins and p.v.c.

Acid conditions occur in the vicinity of, for example, coke ovens, gas works, oil-fired plant, galvanising plant and paper pulp mills, and in these

conditions, cracking is a frequent form of failure; the cracking and peeling in acid environments is usually much more severe and occurs much earlier in the life of the paint film than is the case in other environments. Failure in acid environments results from the specific properties of pigment, medium, or drier used in the paint, e.g. in sulphuric acid environment zinc pigments form zinc sulphate, which appears on the paint surface.

Non-oxidising and weak acids, in contrast to oxidising acids, can penetrate paint films without destroying them; they then react with the metal base to form salts with resultant stresses which cause cracks. Magnesium-rich alloys are particularly prone to attack by acids; their salts, having considerable volume, in severe cases effloresce through the broken paint films.

For resistance to acid conditions alone, traditional filled and unfilled bituminous solutions (which have economic advantages), chlorinated rubber and shellac have been used. Crosslinking coatings, e.g. amine-cured epoxy resins, often blended with coal-tar which develops resistance to oils and solvents, have obvious advantages on chemical plant.

Alkaline Environments

Oil-base (including oil-modified alkyd resin) paint films should not be used in alkaline environments as the paint will deteriorate owing to saponification; alkali-resistant coatings are provided by some cellulose ethers, e.g. ethyl cellulose, certain polyurethane, chlorinated rubber, epoxy, p.v.c./p.v.a. copolymer, or acrylic-resin-based paints. In particular, aluminium and its alloys should be protected by alkali-resistant coatings owing to the detrimental effects of alkali on these metals.

Salt Solutions

Corrosive solutions, e.g. salt solutions as present in salterns, refrigeration plant and sea-water, are particularly active at the water-line (cathodic zone), where alkali may accumulate and creep up between paint and metal¹¹ and cause softening and loosening of the paint. This process may also occur where the metal is completely immersed, particularly below paint films pigmented with zinc or aluminium¹⁵. Caustic soda is formed at the steel surface (which is made cathodic by the zinc) resulting in the softening of oil-base paints and consequent loss of adhesion. In sea-water, at the local cathodes the total concentration of ions will exceed that in the surrounding sea-water, and water may be drawn in by osmosis, with resultant alkaline blistering¹⁵. This is usually the first sign of electrochemical corrosion; alkaline peeling and corrosion of the metal become apparent only later. Good results in the salt-rich Mediterranean have been reported^{16,17} with anticorrosive primers containing a proportion of chromium fluoride, including those for ships' bottoms.

Marine Atmosphere

Iron girders, etc. are frequently supplied to a site in the grit-blasted and primed condition, but occasionally this work is carried out on site. If the structures lie about afterwards for some time in a salt-laden environment, e.g. a marine atmosphere, and are not thoroughly washed with fresh water and dried before further painting in order to remove all traces of sodium chloride, the latter will soon play havoc with the steel and anticorrosive film system. This will occur after erection and possibly even inside buildings owing to under-rusting accompanied by severe blistering and followed by flaking with rustbacking. The rust can be in various states. Analogies can be drawn in connection with the repainting of ships in dry docks. High relative humidity has an aggravating effect.

Corrosion-promoting Pigments

Some pigments promote corrosion owing to their content of soluble salts, their reactivity, or their electrochemical action, and thus should be avoided. Rust of the spotted type can be the consequence of their presence in a paint, especially the first coat, e.g. of graphite (noble to steel), some red oxides of iron, gypsum, ochre or lamp black.

Paint containing potentially soluble copper, such as antifouling compositions, if applied directly to steel, may stimulate corrosion by plating out of copper anodes. Antifoulings are always separated from the steel by an effective anticorrosive primer, but interaction between the two must be avoided by suitable formulation to avoid corrosive and excessive leaching, i.e. making the antifouling ineffective¹⁷. Mercury compounds, used as fungicides or for antifouling can promote rapid attack of aluminium and its alloys under wet or humid conditions.

Effects of Stoving and Storage Conditions

During stoving in convection-type box ovens, drying can be delayed (as it can on air drying when the ventilation is insufficient, e.g. in a ship's hold) if the vents are closed too far, or if the coated articles are too closely packed. In the latter case there may even be trouble caused by solvent wash, i.e. redissolution of the uncured film by stagnant solvent vapours, which occurs mostly on surfaces near the top of the oven. This can lead to the establishment of practically unprotected areas.

Damp conditions contribute to 'gas-checking'* of some synthetic stoving lacquers, quite apart from the effects of foul oven gases, or the presence of detrimental solvent vapours, e.g. from a trichlorethylene degreasing plant.

Overstoving, too, can result in embrittling due to overpolymerising or oxidising, followed by cracking or crazing. Stoving enamels, etc. which are based mainly on cross-linking epoxy resin combinations, behave for all

* A fine or coarse wrinkling due to irreversible swelling of a surface-dried film.

practical purposes in exactly the contrary manner to this, forming almost the only exception to the general rule. They are brittle when undercured and become tougher after complete cure, and even remain so when they have been somewhat overcured. Certain members of this class of coatings, therefore, do not perform too satisfactorily on air drying. It has been observed, for instance, that air-dried amine-cured anticorrosive epoxide paints over new steel were not able to hold down millscale, which appeared still adherent at the time of painting, for any practicable length of time in contrast to the performance of traditional anticorrosive oil paints. Very premature flaking occurred, the brittle paint flakes being backed with millscale. Epoxide resin esters, however, perform quite well, apart from a tendency to chalking.

If infra-red heating or any other radiation curing method is employed, areas which are shaded from the rays or are outside the area of greatest flux density, cannot dry as hard as the fully irradiated surfaces, and may form weak spots susceptible to mechanical damage and consequent corrosion.

After long storage in their packages, certain oxidising, i.e. drying-oil or drying-oil-modified alkyd-resin-based paints containing certain pigments, of which iron oxides, iron blues, toluidine red and carbon blacks are the most important, lose some of their drying properties, probably owing to inactivation of driers by adsorption on the pigment surface, followed by slow deactivation of the adsorbed catalysts¹⁸. Such paints, often used as primers, dry and harden satisfactorily when freshly made, but storage may make them increasingly sensitive to the application of a second coating. Discoloration due to mixing of the films, drag of the brush, and in severe cases even lifting, may result.

Lifting may also occur if a paint containing strong solvents (xylol or solvent naphtha, not to mention such active solvents as esters and ketones) is applied (not necessarily by brushing) over a paint which is not resistant to them. The older an oxidising paint film becomes, the more solvent-resistant it will be. Short-oil media and pigment-rich paints are not so prone to lifting. This type of failure is not restricted to oil-base materials; it can, for example, also occur with chlorinated rubber paints.

Effects of Application Methods

Excessive thinning of a paint of good quality is often the cause of the application of films which are too thin. The temptation for operators to do this is great as it often increases the ease of application and their bonuses, especially in the case of paints for brushing. Overthinning is particularly common when surface coatings based on e.g. medium to short oil-modified alkyd resins, or coatings which dry by evaporation are being used. It is particularly difficult to check with highly opaque aluminium paints.

Overthinning is also frequently responsible for running and sagging, which in turn promotes excessive pigment flotation. If application is by spraying, this can be countered by the use of thinners which evaporate quickly. In brushing, however, such thinners would cause dragging of the brush. If the evaporation rate of thinners is too fast, they may promote

cobwebbing when highly polymerised resins such as the vinyls or chlorinated rubber are being sprayed. Again, if heavy thinners containing strong solvents are used in the second coating, lifting trouble may be experienced in addition to sagging.

Some specially formulated paints can be applied wet on wet by spraying, without the aforementioned disadvantages.

Some water-thinned industrial paints exhibit anomalous viscosity changes during drying and therefore need careful control of air flow and humidity to ensure satisfactory film formation.

If paint is insufficiently stirred before use, over-pigmented paint from the bottom of the container will, when it comes to be used, act as a short-oil non-elastic coating of poor binding power, while under-pigmented mixture from the upper strata will perform more as a longer-oil, more elastic coating, and will possibly run. Two- or three-pack materials mixed immediately before use present special hazards. The supplier's recommendations on mixing ratios and pot life must be followed carefully. Pot life is highly temperature dependent and may be reduced greatly if materials mixed in bulk are heated by exothermic reaction. Thinning of material that has partially cured in the pot results in unsatisfactory films.

If an elastic or insufficiently hard primer or paint has been applied under a less elastic top coat, or if the first coat (or set of coats) of oil-base paint has been second-coated before it is completely dry, not only will the paint-work remain soft for an unduly long period, but cracking will also follow, as the upper layer cannot follow the movement. If the last coat is very thick this fault will frequently manifest itself in the form of alligatoring, i.e. the formation of cracks which do not penetrate all the films down to the substrate, and which may be present in the top layer only.

Repainting

For painted structures it is essential that an additional paint coating be applied as soon as there is evidence of paint breakdown. The Protective Coating Sub-committee of BISRA⁴ recommend painting of steel surfaces when 0.2–0.5% of the surface area shows evidence of rust. Delay in repainting may be a false economy, as if rusting is extensive it may be necessary to clean down to bare metal before paint can be applied.

Should an old bituminous paint layer have to be recoated, this should be done only with another bituminous paint, unless the surface is first insulated with one of the special primers which are available for the purpose. Bleeding and premature checking may otherwise occur.

Damage to prefabrication primers or even the whole film system can be caused on transport or on erection, leaving for example, bare edges. Good supervision is necessary to ensure that defective areas are conscientiously touched-up before applying further paint films. It has been recommended to disregard the coat of prefabrication primer when deciding the number of coats to be specified⁷.

Adhesion Difficulties

It is important to realise that various factors contribute to good adhesion of paint films. These include:

1. Cleanness of the base, i.e. freedom from grease, which improves the wettability of the metal surface, and the removal of oxides, dust or loose paint, etc. already described. The closer the surfaces of paint film and metal, the more secondary valencies originating in the polar constituents of the medium are brought into play.
2. Mechanical pretreatment of the metal by weathering, sanding, shot-blasting¹⁹, etc. for the removal of corrosion products and loose mill-scale, and chemical pretreatment by phosphating, pickling, etc. to create a mechanical, or, in the case of etch primers, a chemical key. Wet abrasive blasting is particularly effective in removing contaminants from rough surfaces. Degrees of cleanliness of steel surfaces can be compared with BS 4232, etc.²⁰
3. Selection of suitable coatings possessing good wetting properties, which are elastic enough to expand and contract with the metal base over a reasonably long period and which, as far as priming is concerned, have an affinity with the metal to be painted. It is often not appreciated that the adhesion properties of a given coating material may vary according to the type of metal to which it is applied, although it is suggested that the degree of retention of contaminants is the real cause²¹.

So far as iron and steel are concerned, the adhesion problem is simple, and the oleoresinous coatings which are generally applied to them form a good bond with them. Mechanical pretreatments are always extremely useful.

Cracking, flaking, scaling or blistering due to under-rusting (the latter often being accompanied by brown discoloration of the film) is, as has already been explained, due to mechanical action by the products of corrosion. This may at times pose the problem of whether the paint or the painting system was responsible for the corrosion, or whether, on the other hand, it was the corrosion (possibly residual) which was responsible for the unsatisfactory performance of the paintwork. The better the adhesion of the paint to the metal, the less damage there will be to the paint film, and the less premature corrosion will ensue. This is similarly the case with non-ferrous metals. Rough (especially blasted) steel surfaces which have received too thin a paint coverage will be indicated by the presence of pinpoint rust spots in the film surface, wherever the metal peaks have not been sufficiently protected.

A patchy form of rust that attacks paint films from underneath, can be caused by sweaty hands, residues from fluxes, etc. Examples of the latter include residues from phosphating and soluble salts (including those from unsuitable rinsing water) and they can manifest themselves on steel in the form of a creeping filiform corrosion, i.e. as progressing threads of rust which loosen the coating. This can be followed visually through transparent films. It occurs, however, only when the relative humidity of the surround-

ings is above 82%, and if oxygen diffuses through the film. Diffusion of carbon dioxide seems, however, to suppress filiform corrosion^{22,23}. A somewhat similar type of corrosion that causes the destruction of paint films as a result of the presence of salts beneath, is termed *filigran corrosion*, and has been observed on painted ships²⁴. Filiform corrosion is considered in Section 1.6.

Aluminium and magnesium alloys, copper and its alloys, and zinc and zinc-base diecastings, including galvanised iron, to name the most important groups of non-ferrous metals, can offer serious adhesion problems. These are aggravated if the surfaces are very smooth, as, for example, on diecastings or hard rolled sheets. For light metals, p.v.b.-based* etch primers are ideal; long-oil alkyd-resin-based zinc chromate primers may also be satisfactory. Etch primers and alkyd-resin-based coatings are very suitable for zinc and its alloys and alkyd resin-based coatings for copper and its alloys. If the first coat has been selected for good adhesion, the subsequent ones may be chosen from a wider range of products to satisfy other requirements involved in the particular application.

A number of cold-rolled alloys based on aluminium, copper and zinc are susceptible in varying degrees to recrystallisation on exposure to heat. This can have a detrimental effect on the adhesion of paint films. While there may, at first, be no sign of trouble, the defect will become obvious by brittleness of the film after some storage time has elapsed.

To avoid peeling of oleoresinous top coats from zinc-rich primers, a sufficient interval should be allowed between coats to permit the zinc-rich primer to weather first; in sheltered conditions soluble products should be removed before recoating.

Lacquers drying by evaporation to rather rigid films, e.g. some nitrocellulose lacquers, may not be able to follow the movements of metals caused by changes in temperature, and rapid cracking, followed by flaking of the paint film, can result. In all such cases the smoother the metal surface, and the less affinity the coating has for the grease- and oxide-free metal surface, the more likely breakdown is. The presence of various proportions of minor constituents in alloys, including those of iron, can have a profound effect on the behaviour of the main metal in this respect.

Reference has already been made to the detrimental consequences which bad weather conditions occurring during or shortly after application usually have on the life and protective value of a film²⁵.

To protect buried metals from premature breakdown it must suffice to say that protective coatings and other methods must be applied against factors such as the effects of galvanic currents, composition of the moisture in the ground²⁶, humus acids, bacteria, etc. (See Section 14.8.)

In conclusion, it should be emphasised that surface coatings which are of the highest quality, and which where necessary have the special protective properties required, should always be used.

Good supervision, careful working, and common sense can contribute a great deal to reduce paint failures and the wasteful work which is necessary to put a job right.

* p.v.b. is an abbreviation for *polyvinyl butyral*.

Paint Adhesion and Corrosion

When corrosion develops on painted steel the question is often raised as to whether corrosion was a result of paint failure or the paint failure was caused by corrosion. Several studies have shown that adhesion forces are reduced greatly after water soaking or even at very high humidity^{27,28} and it has been argued that film detachment by water usually precedes underfilm corrosion²⁹. Against this view others have claimed that those paints known to have reduced wet adhesion, e.g. those based on alkyd resins, are not uniquely, or even especially, subject to underfilm corrosion³⁰.

Several factors should be considered in this discussion:

1. A continuous intact film of water-resistant paint forms an effective electrical resistance to the flow of a corrosion current (a resistance of over $10^9 \Omega \text{ cm}^2$ through the film is easily achieved). Underfilm corrosion can then only occur if a channel of electrolyte connecting anode and cathode can be established by local adhesion failure between the coating and the metal substrate.
2. Localised adhesion failure occurs most easily where broken scale or rust, or deposits of salts, have impeded wetting of the metal substrate by the film-forming constituents of the paint.
3. After major surface contaminants have been removed, e.g. by wet abrasive blasting of hot-rolled structural steel, application of a thin coat of an etch primer greatly reduces the incidence of underfilm corrosion, presumably by eliminating localised areas of poor adhesion. Phosphate pretreatments followed by effective rinsing have a similar effect over cold reduced sheets.
4. Even small traces of certain corrosion stimulants, notably soluble chlorides and sulphates, can maintain a continuing corrosion process under a paint film because the salts accelerate the initial dissolution of ferrous iron (and other metal ions) but are not immobilised in the hydrated oxide corrosion products. Filiform corrosion is the most spectacular example of this phenomenon, but progressive spread, preceded by blistering, is also observed from scratches or other breaks in a coating, for example during salt spray tests.
5. Soluble salts in or under a coating, even if not active corrosion stimulants, can induce osmotic blistering and thus expose underlying metal to possible corrosion³¹. Such salts may be present in a pigment (even some soluble chromates are suspect), may be formed by reaction with basic pigments (e.g. barium carbonate), or by reaction of organic acids from drying oil oxidation with metal oxide substrates (zinc or magnesium formate are especially likely to be found at interfaces with the appropriate metals). Residual salts from rinse water have been shown to cause 'snail trail' blistering and subsequent corrosion under motor car finishes. Fears have been expressed that soluble flash-rusting inhibitors used in wet abrasive blasting could have similar effects, but no problem has been found with the concentrations normally used.
6. Paint stripping by water is most likely to occur from cathodic areas, the phenomenon of cathodic disbonding sometimes observed on steel protected by external anodes or impressed current being a particularly

spectacular case. This failure may involve direct attack on the paint binder by cathodic alkali³², but some workers have claimed that the attack is more often on the metal/paint interface, possibly having more in common with alkali degreasing processes³³.

Overall there is good evidence for the presumption that the best way to avoid corrosion under paint films is to prepare the substrate in such a way as to maximise adhesion and then to apply an insulating film of paint. Provided that the substrate is free from coarse sharp-edged profile the insulating coating need be no more than 100 μm , thick; indeed a very thick film may be more likely to crack or be damaged by external mechanical action. The value of some chemical pretreatments and self-etching primers has already been mentioned; the possible advantages of incorporating specific adhesion promoters in primers have yet to be fully explored.

Long-life Coatings

All organic and some inorganic, coatings are subject to a continuous process of erosion by chemical breakdown to volatile or water-extractable products. The processes involve oxidation, depolymerisation and other bond-splitting reactions. Many of the breakdown reactions are stimulated by u.v. radiation, particularly the high quantum radiation at the short wavelength limit of the sun's spectrum. Some pigments, notably certain titanium dioxide pigments, accelerate breakdown under u.v. radiation; others, such as red iron oxide or metallic aluminium protect by absorbing the radiation, as do specific u.v. absorbing additives. Typical erosion rates for coatings fully exposed to full weathering, facing south in temperate areas are 1–2 $\mu\text{m}/\text{year}$ for white alkyd paints as against 5 $\mu\text{m}/\text{year}$ for the earlier oil-based paints. In tropical areas with more short wavelength u.v., rates may be two or three times higher.

Modification of alkyd resins with high proportions of silicones considerably reduces rates of attack, but the most spectacular extension of life is shown by fluorinated polymers such as polyvinylidene fluoride where erosion rates can be reduced to 0.1 $\mu\text{m}/\text{year}$. If this level of durability can be achieved an initial coating, if firmly adherent and free from any breaks, may often be expected to maintain protection over a metal substrate for the likely life of the structure. The considerably increased first cost, as compared with more conventional coatings, has to be balanced against the probable saving in maintenance costs or consequences of failure.

Acknowledgment A number of suggestions by W. A. Edwards have been incorporated in this Chapter, and these are gratefully acknowledged.

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14.5 Paint Finishes for Industrial Applications

Introduction

Industrial finishing systems are those paint systems that are applied in factories, not in homes, construction sites or shipyards. In factories it is possible to obtain considerable control over all stages of the painting process. The application process may be selected to give accurate control over film thickness. The temperature and time of drying may be chosen to obtain a given throughput of finished articles. Furthermore, a wide range of polymer types are available to give particular combinations of properties to the dry films.

Industrial finishing systems are applied to a wide variety of substrates, the majority of which are metallic, but they are also applied to paper, wood, wood composites, cement products and plastics. Often a high quality of decoration is required, as well as protection from a number of hazards, such as knocks, abrasions, bending or forming and contact with non-corrosive liquids. Resistance to the weather may be required. Outdoor finishing systems, and many others, are also required to protect metal against corrosion.

Finishing Systems: Factors Governing the Choice

It may be possible to decorate or even to protect some surfaces with a single coat or finish, but protection of metal against corrosion always requires a finishing system. A full finishing system will require some or all of the following coatings.

1. A metal pretreatment or conversion coating This is a specially formulated mixture of inorganic chemicals which react with the metal to produce a strongly adherent, corrosion-inhibiting conversion coating, such as a phosphate or chromate, on the metal surface (see Sections 15.2 and 15.3). This coating often provides a better surface than the original metal oxide layer for obtaining good adhesion of the paint layers.

2. *A primer* On metal, the purposes of a primer are to enhance corrosion protection and to give excellent adhesion. The primer will contain anti-corrosive pigments, such as strontium chromate or zinc phosphate, which will slowly release ions that can repair damage or faults in the underlying conversion coating.

3. *An undercoat* This coat is required to provide bulk cheaply and to be capable of being sanded easily to give a smooth surface for finishing.

4. *The finish* This coat is required to provide all decorative properties (colour and gloss) and the main resistance to external damage (e.g. u.v. degradation).

The selection of each of these coatings (or the decision to omit one or more of them) is dependent on a number of factors, which will now be considered.

Painting systems are selected by the manufacturers of industrial articles, advised by their paint and their equipment suppliers, taking into account the following factors:

- the size and shape of the article;
- the physical and chemical nature of its surface;
- the appearance and protection required from the paint;
- the required output rate.

The selection is made in the light of various constraints, such as:

- existing equipment and space;
- money and space available for new equipment;
- acceptable running costs (including paint, energy and labour);
- the maintenance of safe working conditions;
- conformity with regulations on environmental pollution.

Selection is therefore a compromise. The variety of choices available to the manufacturer will now be illustrated by considering how these factors can operate in the selection of finishing systems for metal articles to be protected from corrosion.

Size and shape can have a dramatic effect. The immense size of a jumbo jet immediately rules out any possibility of putting the aeroplane in an oven; the coatings must all dry at ambient temperature. The size and shape also rule out all automated methods of application. On the other hand, flat sheet can be processed on an automated painting line using economical methods of painting, such as roller coating or curtain coating, followed by cure by stoving of by infra-red or electron beam radiation.

If the surface is smooth, then a high quality appearance may be obtained with low film thickness and only one or two coats. On the other hand, a rough casting can only be given a good appearance if the film thickness is built up with surfacer and sanding is carried out before finishing. It may be possible to use an automated application technique, like electropainting, on a casting, but stoving of the paint will be very inefficient with the large amount of metal acting as a heat sink.

A relatively inert surface like tinplate may not need a pretreatment. Zinc, on the other hand, may be pretreated to improve adhesion of the paint

coat. Steel invariably needs thorough cleaning and an iron or zinc phosphate pretreatment for passivation and subsequent optimum corrosion resistance.

Assuming maximum corrosion resistance is required, then an anticorrosive primer will be needed, with best protection coming from a crosslinked epoxy stoving primer. Most other properties are dominated by the finish, which will be based on a high molecular weight-polymer, either linear or (more usually) crosslinked. The precise selection of the polymer depends on the balance of properties required, but will be constrained by the type and rate of curing necessary.

With infinite space, drying rate does not determine output rate, but usually space is at a premium and drying must be hastened, if possible, with heat (or other forms of energy). If heat cannot be used, fast air movement aids solvent removal, and lacquers based on linear polymers or emulsions dry fastest. They do not, however, confer more than limited resistance to solvents.

Increasingly, industrial painters, especially in the USA, are turning to paints of low solvent content to minimise air pollution. These include powder coatings, 100% polymerisable coatings, high solids coatings and water-based materials. These coatings can demand more energy to obtain good throughput, though radiation-curing finishes are both fast and economical with energy.

Methods of Application and Drying

Since these methods are selected by the industrial finisher at an early stage and can, as discussed above, have a major effect on the polymer options available to the paint supplier, they will be discussed next.

Application

The range of application methods available is extremely wide. A number of these are described in Section 14.1 and include: brushing; a wide range of spraying techniques; techniques involving total immersion, such as dipping, electrodeposition and fluidised beds; methods such as flow coating and curtain coating, in which paint is made to flow over the article. Additionally, the techniques of centrifuging and tumbling or barrelling are especially suitable for very small articles. In the latter method, the articles are tumbled in a rotating barrel with just enough paint to coat them to the required thickness. In the former, excess paint is used and the excess removed by centrifugation after coating.

Extrusion coating is ideal for rods, tube and wire. The article is passed through a paint reservoir and then out via a die, which leaves only the correct thickness of paint in place. There are further techniques suitable for flat articles in sheet or web form. Knife coating is ideal for very thin coats, especially on continuous paper or plastic webs. The knife is either a metal doctor blade or a curtain of high velocity air (an air knife) directed onto the surface and it removes surplus material applied previously.

Even more widely used are a variety of roller-coating techniques. In forward roller coating a controlled amount of paint is metered onto the surface of a rubber or gelatine roller rotating such that, at its point of contact with the sheet or web, roller and sheet are moving in the same (forward) direction. Even finer control of thin coatings is obtained if the paint is transferred from gravure cells onto the application roller.

In the coating of continuous metal coils, reverse roller coating is often used. In this technique the web is moving *counter* to the application roller direction, so that the paint is partly wiped off by the moving coil. Shear leads to better flowout. Another type of reverse roller coating is used for the application of stiff paste fillers to chipboard. Application is by forward roller, but this is immediately followed by a reverse roller, which presses the filler into the board and doctors it smooth.

Tumbling and centrifuging are batch processes, but all the others can be included in a continuous line process and, for suitable articles, the process can be fully automated. If the shape of the articles is unsuitable, some kind of hand spraying is usually selected.

A matter of considerable importance in the selection of an application method is its efficiency. Spray techniques are usually inefficient, since many droplets drift past the target and are lost. Even electrostatic spraying can waste as much as 35% of the paint. There is some loss of paint in most methods, but roller coating, curtain coating and electrodeposition are very efficient. Electrodeposition is also a very useful technique where corrosion resistance is important, since it applies a uniform coating over nearly all surfaces of even the most complex-shaped article.

Drying

Lacquers dry simply by the evaporation of the solvent, leaving behind high molecular weight linear polymers which provide the properties of the films. Only air movement is necessary, but heat speeds up the process. For some emulsion paints the process is similar, though heat may be necessary to soften the polymer particles, allowing them to integrate to form a film. For all other types of paint, low molecular weight polymers must be converted into high molecular weight crosslinked polymers by chemical reaction. Many of these reactions are extremely slow below certain threshold temperatures; these temperatures must be exceeded in drying. Other reactions, which proceed slowly at room temperature, are accelerated considerably by heat. There is a third group of reactions which depend mainly on the creation of free radicals, and there are ways of creating these without heat.

In industrial painting throughput rate is critical and drying equipment will usually be needed. This equipment will control the rate of air movement, to remove solvents and/or volatile reaction products, and is also likely to include devices for raising the temperature of the paint film, or creating free radicals within it.

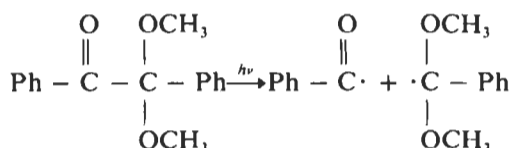
The simplest and most widely used method of increasing the film temperature is to pass the coating through a convected hot-air oven. This is relatively inefficient, but effective with articles varying widely in shape and size. If

the article is flat, speed can be increased by directing jets of very hot air at high velocity onto the surface.

The next most frequently used technique is to raise the film temperature by infra-red irradiation. Emitters vary from low-energy long-wavelength (3.6–8 μm) black emitters (90–500°C surface temperature), through medium wave length (2.0–3.6 μm) red-hot emitters (500–1 200°C) to high-energy short-wave length (1.0–2.0 μm) white-hot (1 200–2 200°C) emitters¹. The radiant energy must be directed to reach all parts of the film; shadowing on complex shapes can cause difficulties. Infra-red heating is often combined with convected hot air.

For specific end uses (e.g. exteriors of small containers) flame drying is a means of very rapidly increasing temperature (0.02–0.04 s). An air curtain surrounding the flame prevents solvent ignition. An alternative, fast method, suitable for simply-shaped metal articles, is induction heating of the metal with conduction to the coating. For removal of water from flat films on non-conducting substrates, radiofrequency heating can be used.

If the film-former is designed to be polymerised by a free radical mechanism, free radicals can be created in the film by decomposing a photoinitiator within the film using ultra-violet radiation²:



The free radicals then initiate curing by attacking residual double bonds in acrylic oligomers and monomers, or in styrene and unsaturated polyester resins. Since most pigments absorb u.v. radiation and can prevent it reaching sufficient photoinitiator molecules, this technique is best suited to transparent coatings or thin pigmented layers (e.g. inks).

Alternatively, the same coatings can be cured by electrons from an electron accelerator without the use of photoinitiators. Electrons from a 150–600 kV accelerator are energetic enough to create free radicals on impact with the polymer molecules and curing ensues. Clear and pigmented coatings can be cured. Electron accelerators are extremely expensive, but are cheap to run.

Both u.v. radiation and electron beam curing are best suited to flat or nearly flat objects, because the beams are directional and shielding must be avoided. Electron beam curing also requires the coating to be in an oxygen-free gaseous atmosphere. Both techniques cure in a fraction of a second and are suitable for fast, high-volume production lines.

Materials and Methods for Various Industrial Finishing Tasks

It is not possible, in a section of this size, to deal adequately with the painting systems used by all industrial finishers. Instead a selection will be covered,

to illustrate the range of problems, finishing materials and methods of application and drying encountered.

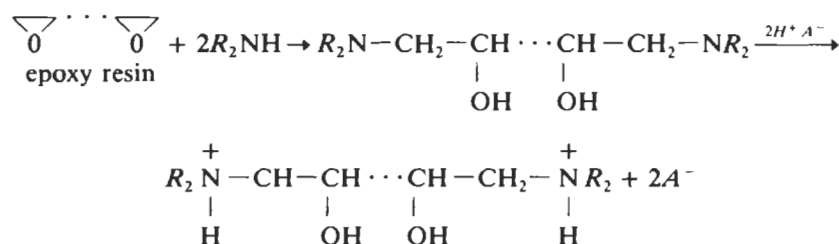
In the sub-sections that follow, there will be frequent references to polymers and resins. Where the detailed chemistry is not shown, it will be found in Section 14.9.

Motor cars: the original finish

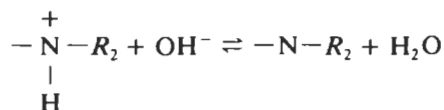
The modern motor car is made from steel, zinc or zinc alloy-coated steel and some plastic parts, all of which require painting. The main component is the body shell, made from the above metals, and this is coated in a continuous production process. A full finishing system with all four coatings is usually applied for maximum protection and a high quality appearance.

First comes the pretreatment stage. After rust removal and alkaline degreasing, a zinc phosphate formulated pretreatment (see Section 15.2) is applied by dip or spray-dip. Crystalline iron-rich zinc phosphate forms on the metal surface at a coating weight of 0.5–4.5 g/m².

After rinsing and dry-off, the primer is applied. In most modern plants this means electrodeposition of the primer (Section 14.1). The most widely used primers are cathodic. The body shell is made the cathode and current flows between it and inert anodes in the electropaint bath. The paint is formulated so that the resin is basic and, when neutralised with an acid such as lactic acid, becomes positively charged. The most widely used resins are epoxy-amine adducts:



The primer contains fine particles of paint in water, each particle being pigmented resin and therefore carrying a positive charge. At the cathode, hydrogen is discharged by electrolysis of water, leaving an excess of hydroxide ions. This pushes the polymer ionisation equilibrium to the right:



The particles therefore lose their charge. Since the charge provides the colloidal stability, the colloidal paint destabilises and deposits on the nearest surface, the car body. Primer coatings 12–35 μm thick are applied according to primer type. Each particle also contains a crosslinker for the resin, usually a blocked isocyanate. After rinsing, the primed article is passed into a hot

air oven at 180°C for about 20–30 min, during which time the isocyanate unblocks and reacts with the epoxy.

After a de-nib, spray surfacer is applied to build up the film thickness before top-coating. The surfacer contains a high level of pigment and extender (at least 35% by volume) and frequently a saturated polyester resin with a melamine—or urea—formaldehyde crosslinker. The coating is applied at thicknesses up to 35 μm and stoved for 20 min at 150–165°C.

Sanding is carried out at this stage and, after clean-up, the final colour or top-coat is applied. There is some variation in the resin chemistry used. Alkyds crosslinked with melamine-formaldehyde are widely used for non-metallic pigmentation. Metallics are usually based on acrylics for better durability. The acrylic may be thermoset with melamine-formaldehyde or a thermoplastic lacquer (plasticised copolymer of methyl methacrylate). A thickness of about 50 μm is applied and stoved for 20 min at 130°C (lacquers receive a bake-sand-bake process for a smoother appearance).

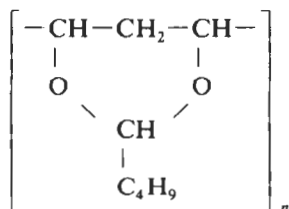
Motor cars: repair finishing (or refinish)

If a motor car has to be refinished after repair, commonsense suggests that the original finishing system would be ideal for maintenance of protection and durability. However, with tyres, upholstery, fabric and plastic trim fitted and petrol in the tank, the use of such high stoving temperatures is not practical. The practical upper temperature limit is 80°C. This means that none of the original materials is suitable, not even the acrylic lacquer, since this is designed to be sanded and the scratches 'reflowed' at 155°C.

A range of lacquer and low-bake thermosetting materials is available and, since many refinishers are small operators with no oven facilities, all of these materials have to be capable of drying at room temperature.

For a complete panel replacement, the refinisher starts with a panel pre-primed in the appropriate stoving primer. For spot repairs or larger repairs without replacement of metal, there will be areas which have to be rubbed through to clean metal. Any indentations then have to be filled with a stopper or spray filler, probably based on unsaturated polyester resins and styrene, with cure initiated by mixing in an organic peroxide. After sanding, remaining bare metal areas are sprayed with a two-pack etch primer.

Etch primers partially fulfil the roles of both pretreatment and primer. They contain phosphoric acid for surface passivation and are based on polyvinyl butyral:



This provides excellent adhesion to the metal. The PVB will crosslink in the presence of the acid with phenolic resin, and epoxy or epoxy ester resin

may also be included. Zinc tetroxychromate anti-corrosive pigment is an essential part of the pigmentation, since it contributes to a zinc phosphate conversion layer by reaction with phosphoric acid and additionally provides chromate passivation.

After the bare metal is primed, the whole area is built up with primer-surfacer. After light sanding where necessary, the repair is completed with topcoat. The materials used in the primer-surfacer are matched to the selection of topcoat. Topcoat is chosen from four main types.

Two of these types are lacquers, giving quick drying to the dust-free state at ambient temperature, but at the expense of lower film build. Nitrocellulose-based lacquers are preferred in some European countries and acrylic lacquers in North America. Nitrocellulose is plasticised with non-drying alkyds, polyester and liquid plasticiser. Acrylics are plasticised internally by use of plasticising monomers with methyl methacrylate and by solvent plasticiser. Acrylics give better durability and nitrocellulose gives easier application.

With these lacquers, nitrocellulose-based primer-surfacers are used. As well as liquid plasticisers, a wide range of materials are used as plasticising resins: short oil alkyds, maleinised oils, ester gum, rosin and bodied castor oils. Pigmentation is usually inert. Thermoplastic acrylics are often preferred under acrylic lacquers; these are based on acrylic resins and cellulose acetate butyrate.

The other two main finish types are thermosetting enamels. The older enamels are based on quick drying short oil alkyds which dry by oxidative drying. Alternatively, a second component containing either melamine formaldehyde or polyisocyanate may be added to give cure with heat. Higher film thicknesses can be obtained, but drying to the dust-free stage is slower, polishing properties are poor and the enamel may be sensitive to solvent attack if recoated. Nitrocellulose or alkyd primer-surfacers are used.

In recent years the two-pack acrylic/polyisocyanate finishes have gained ground widely, giving a good balance of properties, including excellent durability. Heat is preferred for drying if available. These finishes are widely specified by motor manufacturers for repair of damaged cars which are still under corrosion warranty. Primer-surfacers may also be acrylic/polyisocyanate-based, or alternatively the acrylic resin may be replaced with alkyd or polyester. Whereas aliphatic polyisocyanates must be used in the topcoats for good colour and durability, aromatic polyisocyanates can be used in the primer-surfacer for fast cure and economy.

Coil Metal for Exterior Cladding

This is steel or aluminium sheet made in a continuous ribbon and wound tightly onto a bobbin to form a coil of metal. On a coil finishing line, the coil can be fitted at one end, and wound up pretreated, primed and finished on both sides at the other end. Sheets of painted metal can be cut from the coil and formed for use as the exterior cladding for, for example, industrial buildings and caravans.

There are some similarities between coil finishing and original motor car finishes: both are required to give good exterior durability and both can be

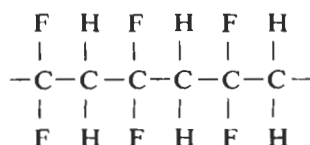
dried at high temperature. There the similarities end. Because coil is a continuous web, the finishing process can be completely automated and carried out at high speed with extreme efficiency. Lines run at 30–200 m/min and this means that stoving temperatures must be very high and times very short (15–60s) if ovens are not to be excessively long. Temperatures peak at 180–250°C just as the coil leaves the oven and the paint is then crash-cooled by water spray.

The first stage is a cleaning and spray-applied or immersion pretreatment process. If the metal is hot-dipped galvanised steel, a complex metal oxide pretreatment may be applied, followed by a passivating chromate rinse, to improve paint adhesion and inhibit 'white rust'. After drying, primer is applied by roller coater at a thickness of about 5 µm. Epoxy resin cross-linked with amino resin is often preferred and chromate pigmentation is used. Application is followed by stoving, quenching and topcoat application at a thickness of 20 µm, again by roller coater. The coil is then passed through another high-velocity hot-air oven, followed by quenching and cooling, and is then wound up.

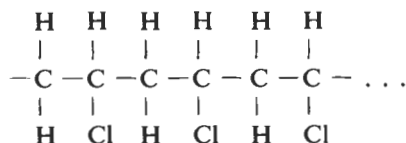
For industrialised buildings long life is required and coating systems are expected to be more durable than those on motor cars, even though paint thicknesses are lower. For this reason, the lowest durability type offered is the thermosetting acrylic (7 years). Longer life can be obtained from polyester resin crosslinked with hexamethoxymethyl melamine (10 years), siliconised polyester with the same crosslinker (12–15 years) or polyvinylidene fluoride/acrylic (20 years). Alternatively, cheaper PVC plastisol can be applied at a thickness of 100–250 µm to give a very damage-resistant coating with a life of 10–15 years.

The back of the coil is simultaneously roller-coated at each station (if necessary) with a 10 µm coat of polyester-melamine backer or a 3–5 µm coat of primer and 8–10 µm of backer.

The very high durability of PVF₂ comes from the polymer structure:

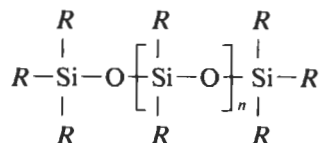


This material does not absorb u.v. radiation at all and so is not degraded by sunlight. The structure of polyvinyl chloride is quite similar:



However, this structure does not give the same properties, and the polymer degrades slowly, eliminating HCl. Plastisols (PVC + plasticiser) lose gloss rapidly and gradually chalk even in temperate climates, but the high film thicknesses that lower cost permits lead to long life.

The increased durability obtained by siliconising a polyester resin comes from reacting a high hydroxyl value polyester with 20–30% of appropriate silicone resin.



where $R = -O-CH_3$ or $-O-Ph$

Agricultural equipment

Tractors, combined harvesters, ploughs, harrows, etc. are large and complex machines with many parts. Some of these are sheet metal and others are castings, and all are mainly steel. The assembled product is finished in a uniform single 'house colour' of the manufacturer, even though the parts may be painted with different systems in different finishing shops.

Like coil and motor cars, agricultural equipment must have exterior durability, though the main emphasis is placed on showroom appearance. However, because of the variety of components and systems, some are air dried, some force dried and some stoved at temperatures varying from 15°C to 150°C. Short-medium oil alkyds are used for these coatings, with driers at ambient temperature or force-dry temperatures (60–80°C) and with amino resin crosslinkers at stoving temperatures (120–150°C). Relatively high solids can be obtained, leading to the full-bodied glossy appearance required at lowest possible cost.

Parts are normally degreased, but not pretreated. Primers are applied to critical areas, but much of the metal receives only topcoat. Primers and one-coat finishes are applied by dipping, electrodeposition or flow coating. Waterborne alkyds are increasingly used, for reduced fire hazard and lower environmental pollution. Water solubility or dispersibility is achieved by making alkyd molecules with higher concentrations of acid end-groups; these are neutralised with ammonia or amines to a pH value of about 8. In such alkaline media, hydrolysis of the polymer's ester linkages can occur rapidly, and storage life has to be extended by the use of more expensive hydrolysis-resistant acids and alcohols (e.g. 5 or 6 carbon diols, shielded hydroxyls, as in neopentyl glycol, and isophthalic rather than *o*-phthalic acid³). Some water-miscible solvent is also necessary.

Topcoats over primer are often applied by airless spray. Trends to higher standards of exterior durability have encouraged the use of methacrylated alkyds and two-component urethane finishes.

Aircraft

This is the last of the end usages in this section for which exterior durability is required from the painting system. The substrate here is mainly aluminium

alloy in various forms. The aircraft is constructed from many components and where possible these will be coated at least as far as primer before the aircraft is assembled. Protection from corrosion is a major requirement. Chromic acid anodising and chromate conversion coatings (Section 15.3) are used at the pretreatment stage and these are followed by two-pack epoxy-polyamide (or polyamine) primers, which will cure at ambient temperature. The primers contain leachable chromate pigments for maximum corrosion protection.

From the topcoat a number of properties are required. First, a high-gloss quality appearance at least as good as that obtained from motor car finishes. Next, u.v. resistance, including resistance to the more destructive shorter wavelengths emitted by the sun which are usually screened out by moisture in the atmosphere, and resistance to extremes of temperature, varying from -50°C in flight to over 70°C on a tropical airstrip (due to absorption of energy by the paint film, especially in darker colours). A special requirement is resistance to the aggressive phosphate ester hydraulic fluids used in aircraft.

These requirements are usually met with two-pack paints based on hydroxyl-rich polyester or acrylic resins in the pigmented pack and aliphatic polyisocyanates in the activator pack. Cure with this type of finish is relatively fast and complete even at low ambient temperatures. An alternative finish is an acrylic lacquer, similar to the lacquer used for refinishing motor cars. These finishes are applied to the assembled aircraft by operators protected by air-fed hoods and using airless or conventional spray guns. High durability pigments are included.

Domestic Appliances

The key properties here are hardness and wear resistance, ability to stand minor knocks and dents without cracking and resistance to various domestic chemicals. These vary with type of appliance, e.g. detergent solutions are important for washing machines, while a fridge will be required to withstand fruit juices, ketchup and polishes. Good colour and appearance in white and mainly pastel shades will be expected. Corrosion resistance is required, especially for washing machines, and domestic appliances frequently have to withstand humid conditions in kitchens.

Good quality steel is used and electrozinc is preferred for washing machines. Steel is pretreated with iron phosphate for economy; electrozinc with a fine crystal zinc phosphate. No primer is normally used: 25–40 μm of finish is applied direct to metal. The required properties are best obtained with a thermosetting acrylic or polyester/melamine-formaldehyde finish. Self-reactive acrylics are usually preferred; these resins contain about 15% *N*-butoxymethyl acrylamide ($\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\text{CH}_2-\text{O}-\text{C}_4\text{H}_9$) monomer and cure in a manner similar to butylated melamine-formaldehyde resins. Resistance or anti-corrosive properties may be upgraded by the inclusion of small amounts of epoxy resin. Application is usually by electrostatic spray application from disc or bell. Shapes are complex enough to require convected hot-air curing. Schedules of 20 min at $150\text{--}175^{\circ}\text{C}$ are

obtainable with the use of *p*-toluene sulphonic acid (or blocked PTSA) catalyst.

A very high quality finish can be obtained with little or no organic emission if the liquid coatings are replaced by a powder coating. Powder coatings are paints in powder form, with a particle size range from 10 to 80 μm . Each particle contains all the pigments necessary to give the colour, the film-forming ingredients and the additives. Milling of pigment is done in an extruder under polymer melt conditions, with all other ingredients present. Extruded paint is then rolled into sheet, broken up into flakes and then ground to powder in a pin mill. Classification is necessary to reject ultra-fine and coarse particles.

For this use, the preferred powders are based on acrylic, epoxy or polyester and epoxy resins. For best colour, epoxy resins are crosslinked with anhydrides of dicarboxylic acids in the straight epoxy coatings, or with saturated polyesters of high acid content in the epoxy-polyester type. Acrylics contain epoxide rings via, for example, glycidyl methacrylate ($\text{CH}_2=\text{C}(\text{CH}_3)-\text{CO}-\text{O}-\text{CH}_2-\text{CH}-\text{CH}_2$), and these groups crosslink

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by reaction with carboxyls in diacids or other acrylic molecules.

The powder for this use is applied using electrostatic guns and, since the transfer is not very efficient, unused powder is recovered in a cyclone. Curing times are around 15 min at 170–190°C.

Yet another option for domestic appliances is to make the appliance from precoated coil. The appliance has to be designed to minimise the problem of unprotected cut edges. Electroplated zinc-coated steel, pretreated, primed and finished with special polyester-melamine, is used. The finish is designed to be hard at room temperature, yet accept bending and forming, probably, but not necessarily, at somewhat higher temperatures (ca. 60°C).

Heating and Ventilating Equipment

Ducted hot air heaters or airconditioners are made largely from sheet metal and finishing systems are similar to those for domestic appliances. Alkyd-amino resin finishes will usually give sufficiently good performance, since resistance to household chemicals is not important in the specification. However, European panel radiators are made largely from cast metal, though corrugated sheet metal is often welded to the back, or between panels, to create a larger, 'extended' surface from which convection can occur.

For these radiators, a finish able to withstand knocks and to accept repainting by decorative house paints is required. A painting method that gives good coverage of the complex shapes of extended radiators is also required. After degreasing and pretreatment with iron phosphate, the finish is applied by electrodeposition or by dipping in a waterborne coating. Acrylic or polyester finishes are applied, usually anodically if by electrodeposition. For even better appearance, the dip layer is a primer and this is followed by an electrostatically applied liquid polyester-melamine or by a powder coating.

Cans

Cans are used for packaging in a wide range of industries. The market divides into three main sectors: beer and beverage, food and general line (covering a multitude of usages outside food and drink). Cans are made from several metals, principally aluminium (especially in the USA), tinplate (especially in Europe) and tin-free steel (steel with a chromium/chromium-oxide coating). Part or all of the can may be made from flat sheet or coil. The body is often drawn from metal discs and this may be done before or after painting. Interior coatings for food and drink have to conform to stringent food regulations and have excellent resistance to the can's contents. Exterior coatings are more concerned with appearance, ink acceptance, resistance to machine handling and to processing. This is a very wide range of requirements, so this section concentrates on the interior usages, with their main requirement for corrosion resistance, and mainly on beer and beverage containers.

These containers are commonly of a two-piece design: body plus end. The body is made from aluminium or tinplate by drawing from a disc and then wall-ironing to stretch and smooth the metal further. The coating is applied by airless spray into the revolving body and must protect the metal from attack by contents which are often acidic. However, once the end is sealed in place, the pack is under carbon dioxide pressure and virtually anaerobic. Under these conditions it has been found that satisfactory protection is obtained from 3–4 μm of a waterborne acrylic-modified epoxy resin clear coating on aluminium. On tinplate, the wall ironing exposes a high proportion of steel and higher coat weights are needed: 5 μm for beer and up to 11 μm for soft drinks. Coatings must be completely continuous and lacquers are tested for pinholes in an electrical conductivity test. Drying is by convected hot air: 3 min in the oven, with one minute at the peak temperature around 200°C.

The epoxy-acrylic resin referred to above is a graft copolymer prepared by the polymerisation of acrylic monomers in the presence of the epoxy resin in such a way that grafting of the acrylic onto the epoxy takes place. Water dispersibility is achieved by neutralising carboxyl groups in the acrylic polymer chain with ammonia or amine. Amino or phenolic resins are used as crosslinkers. Alternatively, solvent-borne epoxy-amino or epoxy-phenolic lacquers can be used.

Two-piece food cans may be made by a draw-redraw process, in which lacquer is first applied to and cured on sheet. Blanks are then cut from the sheet and the can is drawn from the blank in two or three stages. The lacquer deforms with the drawing process and lubricates the draw. It then becomes the interior protective coating. Although epoxy-phenolic solvent-borne lacquers are used, even better drawing properties are obtained from organosols. These are dispersions of colloidal polyvinyl chloride powder in solutions of other mixed resins in solvent, e.g. chosen from epoxy, polyester, vinyl and phenolic.

Wood and Paper

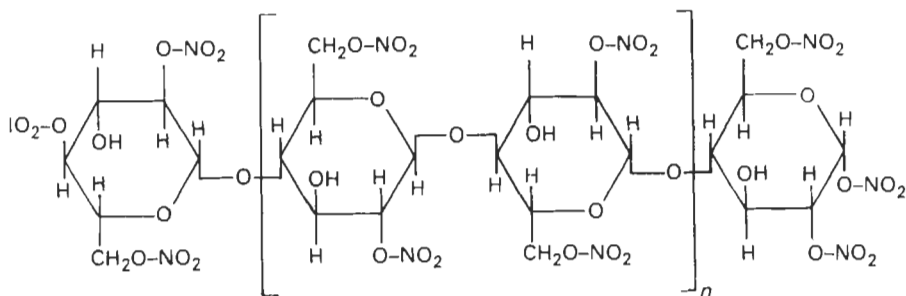
This is the one example in which metal is not the substrate. Corrosion takes on a new meaning; the coating here is required to protect the substrate from direct attack by 'corrosive' substances, from water to more powerful household or industrial chemicals, such as grease, alcohols and bleach. We are concerned with the industrial application of thin protective layers to paper (e.g. labels), card (e.g. playing cards) and many wooden articles, including industrially finished doors, window frames and, particularly, furniture.

Most paper and card finishing operations require only a finish (though, two coats may be needed), while wood may require a primer for sealing the porous surface and then fillers and undercoat to level grain and build up thickness before the topcoat. These operations have the common need to dry the coating without damaging the sensitive substrate. This may be done with cool conditions (room temperature to 60°C), fast air movement and relatively long times, or by short bursts of heat from high velocity hot air or infra-red heaters. Alternatively, curing may be brought about by ultraviolet radiation or electron beams.

Coating materials may be based on short or medium-oil alkyds (e.g. primers for door and window frames); nitrocellulose or thermoplastic acrylics (e.g. lacquers for paper or furniture finishes); amino resin-alkyd coatings, with or without nitrocellulose inclusions, but with a strong acid catalyst to promote low temperature cure (furniture finishes); two-pack polyurethanes (furniture, flat boards); unsaturated polyester resins in styrene with free-radical cure initiated by peroxides (furniture); or unsaturated acrylic oligomers and monomers cured by u.v. radiation or electron beams (coatings for record sleeves; paperback covers, knock-down furniture or flush interior doors).

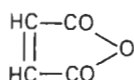
These coatings are applied by spray on more complex shapes, but on flat sheet or board roller coating is the preferred method, with curtain-coating used for thicker layers.

Nitrocellulose, of the resins used in these end uses and in car refinishing, is the nitrate ester of cellulose. The structure is linear and a wide range of (high) molecular weights is available as well as various degrees of nitration:

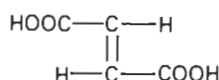


A cellulose nitrate

Unsaturated polyesters are similar to the saturated polyesters shown in Section 14.9, but include maleic anhydride or fumaric acid to introduce unsaturation:



Maleic anhydride



Fumaric acid

Unsaturated acrylic oligomers are made from unsaturated acrylic monomers. For example, an epoxy acrylate may be made by reaction of acrylic acid with epoxy resin.

Newer Developments

The pressures leading to new developments in industrial painting derive from the drive for better quality, the need for economy, and the demand for increased safety in the workplace and in the environment.

Better quality Nowhere is this more evident than in the motor industry, where warranty times for corrosion protection have steadily lengthened. There is a target towards which the industry is moving of a '10-5-2', warranty, i.e. a 10 year guarantee against perforation, a 5 year guarantee against cosmetic corrosion damage on the outer face of the metal and a 2 year guarantee against corrosion at edges. To achieve this, more and more of the car body steel is coated with zinc or with a range of zinc alloys. In Japan, some of these alloys are delivered to the car manufacturer already coated with a conversion coating and a 1 μm organic coating, for greater protection for those parts which cannot at present receive paint. These changes have created many new difficulties and challenges for pretreatment process suppliers and paint suppliers alike. New multi-metal pretreatments are becoming available, and more versatile electropaints are required.

Economy Economies can be achieved in various ways: lower cost paint, fewer painting operations, less paint, faster throughput, more automation and less energy for cure. Pressures continue on paint suppliers on all these fronts. Attempts are being made to extend the etch primer principle to uses other than refinishing by developing primers that also have a pretreatment action. The most widespread pressure is to bring stoving temperatures down, and decreases of 10-30°C have proved possible in many end uses. Alternatively, much greater throughputs are being required without temperature reduction to increase line capacities. An interesting process, which eliminates heat altogether, is the vapour curing process. In this, isocyanate-containing coatings are cured rapidly by exposure to catalytic amine vapour at ambient temperature.

Safety No year goes by without some widely used chemical being declared suspect on toxicity grounds. The paint industry has responded rapidly to eliminate toxic chemicals from coatings or to show how they can be used safely in an industrial environment. Examples are the elimination of specific ether-alcohol solvents and the introduction of air-fed hoods for spraying isocyanates. Of particular interest in corrosion prevention is the current pressure to eliminate chromate pigments. Currently there are no equally effective alternatives and the emphasis has had to be on safe usage. The search for replacements continues.

Pollution of the environment is increasingly regarded as undesirable and the trend over the last 15 years to change to less polluting coatings (water-based, higher solids, 100% polymerisable and powder coatings) will continue. Where lower solids solvent-borne coatings are still necessary, after-burners are often installed to burn the solvent fumes and recycle the energy released. Waste disposal problems with chromate pretreatments are being minimised by the introduction of 'no-rinse' or 'dried-in-place' pretreatments, which are roller coated onto flat metal surfaces, with virtually no waste.

G. P. A. TURNER

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14.6 Paint Finishes for Structural Steel for Atmospheric Exposure

Paint for structural steelwork is required mainly to prevent corrosion in the presence of moisture. In an industrial atmosphere this moisture may carry acids and in a marine atmosphere this moisture may carry chlorides. Paint is therefore required to prevent contact between steel and corrosive electrolytes, and to stifle corrosion, should it arise as a result of mechanical damage or breakdown of the coating through age and exposure.

For an adequate barrier against moisture, sufficient thickness of paint must be applied. The modern trend is to apply high-build coatings based on media having high intrinsic water resistance. Such paints may be pigmented with corrosion inhibitors or minerals which impede the flow of moisture through the film.

Correct surface preparation is of paramount importance. High performance paints will almost certainly fail if applied over badly prepared surfaces whilst simple, low performance coatings may perform surprisingly well over correctly prepared surfaces. Good adhesion is essential and the biggest single factor in good adhesion is good surface preparation.

Methods of Preparing Structural Steel

Degreasing

The first stage in any method of surface preparation is to ensure that any oil or grease is removed, otherwise the preparation method is likely to spread the contamination over a wider surface. Large quantities of oil or grease should be physically removed by scraping, and then the rest is best removed by emulsion cleaners, followed by thorough water rinsing. Under site conditions, degreasing by wiping the surface with solvent is not recommended because this invariably leads to the spreading of a thin film of oil over a wider area. In a factory, however, solvent vapour degreasing can be a very effective process.

Manual, Wire-brush and Mechanical Methods

Cleaning with mechanical or hand wire brushes, grinders, chippers or scrapers rarely removes millscale, paint or other tightly adhering contaminants, or traces of rust or deposits in pits and crevices. Results can be very variable and the process must generally be a relatively slow one in order to be effective. On the other hand, for very heavily rusted surfaces, initial chipping and scraping can save time by removing loose, heavy deposits before more thorough surface preparation methods are employed. Photographs of different levels of hand cleaning are included in the British Standard 7079:Part A1:1989, St Series¹. Since wire brushing as a method of surface preparation is unlikely to remove much contamination, the old practice of 'weathering' beforehand should be avoided if possible. It can only result in the transformation of new steelwork, with its admittedly undesirable millscale, into corroded and pitted steelwork, with corrosion products which are even more undesirable and difficult to remove.

Dry Abrasive Cleaning

This is the most important and most widely used mechanical method of surface preparation. Originally, sand was used as an abrasive but now, because of the hazard to health, it has already been replaced in the UK by metal or non-silicon materials. There are two main types of process.

In the first, the abrasive (generally a non-reusable, non-metallic type) is carried by a jet of compressed air through a hand-held nozzle. In the second, the abrasive (generally round iron or steel shot) is thrown centrifugally from rotating impellers in a fixed plant. Both types are suitable for factory work but compressed-air blast-cleaning systems are more versatile and are most commonly used for on-site cleaning. Smaller blast-cleaning equipment incorporating a vacuum at the head to collect the abrasive is also available. This is slower in use than the conventional system but it can sometimes be used in situations where open blasting is not possible. It is particularly useful for small-scale repair work.

Photographic standards and written descriptions of various stages of visual cleanness of steel surfaces after surface preparation by blasting are available in British Standard 7079:Part A1:1989, Series Sa¹.

Wet Abrasive Cleaning

High-pressure water jetting can be a dangerous process. Also, it is not a very efficient method of cleaning a surface for painting. The addition of an abrasive, generally sand, to the water gives a considerable improvement in cleaning. There are now even more effective wet processes using low-pressure water added to a high-pressure air stream containing sand. Since all wet processes leave wet surfaces these will soon form a powdery film of rust which, although generally iron oxide rather than iron sulphate or chloride, would be an undesirable surface to paint over because of its powdery nature. Some wet processes use inhibitors in the water to prevent such rusting, but it is

important to establish that any traces of such inhibitors will be compatible with the subsequent paint finish. The inhibitors themselves are obviously water soluble and if left in quantities on a clean surface would be another cause of subsequent breakdown.

Flame Cleaning

In this method an oxyacetylene or oxypropane flame is passed across the steel. The sudden heating causes millscale and other rust scales to flake off as a result of the differential expansion between the scale and the metal. In addition, any rust present is dehydrated. Immediately after the passage of the flame, any loose millscale and rust that remains is removed by wire brushing. This generally leaves a powdery layer which must also be removed by dusting down.

Acid Pickling (Section 11.2)

Pickling as a method of surface preparation is generally carried out by immersing the steel in an acid bath and then rinsing with clean water. It is essentially a works process because it must be carefully controlled. Site application of acid washes, etc, is not recommended.

Types of Paint (Section 14.2)

Protective coatings are usually applied as systems. The simplest system would be:

- (i) A primer in contact with the metal. This usually contains a corrosion-inhibiting pigment, capable of stifling either the anodic or the cathodic reactions in electrolytic corrosion.
- (ii) Finishing coats capable of adhering to the priming coat, resisting the ambient exposure conditions and providing the necessary decoration, light reflection, etc. where necessary.

It is usual to define primers in terms of the principal inhibiting pigment e.g. zinc phosphate, zinc dust or zinc chromate, and the topcoats in terms of the binder, e.g. alkyd, chlorinated rubber, etc. This practice can be confusing, however, and lead to the selection of incompatible coatings.

The paint system needs to be chosen carefully for demanding environments, particularly marine situations.

In general, interior steelwork is exposed to less severe conditions than exterior, but in some chemical factories the reverse is true and here special types of paint are needed. Much structural steel is encased in concrete; it is therefore hidden from view and is given some protection while the concrete remains alkaline. Where the concrete is thick, corrosion may be delayed, but as the concrete becomes carbonated and particularly if it is penetrated by acidic rain water, the metal will corrode. In general it is advisable that steel which is to be encased in concrete, especially for industrial plants, should

be prepared by one of the procedures outlined above and coated with an anticorrosive alkali-resisting composition.

Air-drying Paints

The selection of paint is a matter for the expert, but some knowledge of composition is of help to the user. Paints based on the drying oils, usually linseed and tung oil, are still used for decoration and protection, though the traditional oil paints have been superseded by those based on synthetic resins. Of these the alkyd resin and phenolic resin paints are the most widely used because they have excellent durability. The normal decorators' paints, however, do not have the necessary resistance to chemical attack required for protecting steelwork in industrial conditions. Alkyd paints, for instance, are sensitive to alkali and are frequently softened and degraded by prolonged exposure to hot steamy conditions. Alkali formed locally at the cathodic area of a steel surface may destroy the adhesion between such paints and the metal.

A high degree of resistance to water and chemical attack is provided by some oil-based paints, notably those based on tung oil and pure phenolic resin, but for the greatest resistance to these forms of attack, oil-free paints are recommended. Of these, bitumen is widely used, because it is cheap. Bituminous coatings fulfil an important rôle in protecting hidden steelwork, where appearance is of little account. In recent years there have been considerable advances in the technology of bituminous compositions, and heavy-duty compositions now available give hard, tough coatings which can withstand rough handling without damage and virtually exclude all water from the steel.

Chlorinated rubber-based paints have the advantage of combining acid and alkali resistance with weather resistance and decorative qualities. Highly impermeable anticorrosive systems can be built up and these paints have been used with great success to protect industrial plants where low maintenance costs are needed. The alkali resistance of chlorinated rubber paints makes them suitable for protecting concrete where it is desirable to safeguard embedded steel from corrosion. Chlorinated rubber finishes are now also available as high-build coatings and the combination of high intrinsic resistance with thickness provides excellent protection.

Chemically Cured Paints

These are supplied as separate components which are mixed together and then applied. The paints cure by chemical reaction—a process which also occurs in the can and so limits the time available for application after mixing. The films are tough and have good chemical resistance. There are three main types of these coatings:

- (i) Epoxy resin-based materials, which are cured with amino compounds or their derivatives.

- (ii) Polyurethane coatings which cure by the interaction of polyisocyanates with hydroxylated resins.
- (iii) Polyester resin finishes which cure by peroxide-stimulated polymerisation.

All these materials are capable of giving durable coatings. The epoxide resin finishes are highly resistant to alkali and acid and, like the other chemically cured finishes, are resistant to a wide range of oils, greases and solvents. They are used for protecting steelwork. The adhesion of paint to steel is good if proper attention is paid to preparation of the surface and if due attention is given during formulation to the ultimate structure of the cured film. In this respect both curing agents and solvents play a significant part.

Thick Coatings

Chemically cured coatings differ from air-oxidised coatings in that they dry throughout the film regardless of thickness. In thick films, oil paints may not cure satisfactorily. The chemically cured materials lend themselves to protective coatings of considerable thickness with the consequent advantages of good performance and long life, and they have contributed significantly to the protection of steel in corrosive conditions. It is possible to apply high build systems which equal in thickness and performance many coats of orthodox paints, with consequent savings in labour costs. The extra cost of materials is more than compensated for by savings in time and application costs, and where scaffolding and shut-down time are involved this may be a matter of great importance. Quite apart from the economic advantage of thick films, the lower the solvent content the lower the intrinsic permeability to moisture and aggressive ions. Solvents, particularly polar solvents as used in many polymer resin-based paints, influence the structure of films over the early weeks of their life. Small quantities of many solvents are retained in the cured films for a long time, and water and aqueous solutions are able to penetrate the solvated films more easily.

The Paint System

The priming coat provides the bond between the metal and subsequent coats. It gives electrochemical control of corrosion. Adhesion is dependent largely on the nature of the binder and the cleanliness of the metal surface.

The pigment is the principal agent in the electrochemical control of corrosion by primers (see Section 14.3). Probably the best known anticorrosive pigment is red lead. When used in conjunction with linseed oil as the binder it gives very good primers which will perform well over relatively poorly prepared (manually abraded) steel surfaces. Present-day use of red lead (and lead pigments, generally) in paints has been drastically curtailed as a result of understandable pressure from the environmentalists.

Zinc chromate and zinc tetroxychromate have also been used successfully in anticorrosive paints. Both pigments function by releasing chromate ions which passivate the steel surface. In common with lead pigments, those

based on chromates are now also under toxicological suspicion and their use in paints has declined significantly.

In the United Kingdom, zinc phosphate has been the mainstay of many anticorrosive primers in recent years. It can be incorporated into most binders and primers can be manufactured in a range of colours because of its transparent nature. The mechanism of protection is still uncertain. Metallic zinc is also used widely in anticorrosive primers and zinc-rich paints are considered by many to afford best protection. Initially, the zinc protects the steel by galvanic action but, with time, zinc salts form an impermeable barrier and provide a second, reinforcing mode of corrosion protection. For effective galvanic protection, high concentrations of zinc are required (more than 90% by weight of zinc in the dry paint film) and the steel must be cleaned to a high degree in order that the zinc may be in intimate contact with the substrate.

The search for new, effective anticorrosive pigments with low toxicity to replace red lead and chromates in paints has occupied the attention of many paint-making companies recently. Barium metaborate, calcium molybdate and zinc molybdate have been identified as possible compounds but they have not found general acceptance in the United Kingdom and western Europe, most probably because of their lower cost effectiveness.

Welds on steelwork need special attention because of the different composition of weld metal and adjacent steelwork, the rough surface and spatter caused by welding and the presence of welding flux. The latter is often alkaline and destructive to many paints. It is necessary to clean thoroughly, preferably by reblasting for 25–50 mm each side of the weld, bare the rough metal and wash off residual flux. The cleaned surface should then be stripe coated with the primer used on the remainder of the surface.

Methods of Application (Section 14.1)

Paint is applied to structural steelwork most commonly by airless spraying. This method of application is particularly well suited to high build coatings where the combination of rapid working and great film thickness allows work to be completed quickly and cost effectively. Application of paints by brushing is still often used for maintenance painting programmes involving small areas.

The weather has an important effect on the drying of paint and on subsequent performance. Paint applied in bad weather may be slow to dry and remain susceptible to damage by rain and fog for a long time. Heavy steelwork has a large heat capacity and follows temperature changes of the ambient air only slowly. Careful consideration of weather conditions and planning of work is frequently repaid by improved results. With new construction there is much to be said for applying the primer and intermediate coats of a paint system at works and applying only the finishing coats on site.

Economic Considerations

The costing of painting structural steelwork is a complex subject. The main items of costing are:

1. Scaffolding.
2. Labour, which may be further subdivided into surface preparation and application labour charges.
3. Materials.
4. Supervision and transport.

The proportion of the whole contributed by each of these items will vary with each job, but it will be immediately apparent that the cost of scaffolding and labour far outweighs the cost of materials and supervision. Therefore even a large increase in the cost of the last two items will produce only a fractional increase in total cost. On the other hand, first-quality materials and rigid supervision will give greatly increased protection and the best value from the expensive items of scaffolding and labour. It is economically sound to consider not only the initial cost of protection, but also the annual cost over the life of the structure, taking into account initial work, maintenance charges and the cost of shutdown. It is now widely recognised that high-quality initial preparation and protection leads to reduction of total costs on an annual basis.

Maintenance Painting

All the foregoing has been concerned with the initial protection of steelwork, but there is far more maintenance painting than new work. The same principles apply to maintenance painting, with the exception that it is often only in isolated patches and in complicated situations, such as around flanges, etc. that the steelwork is bare of paint, and then it is frequently heavily contaminated with corrosion products. The first necessity, therefore, is to clean down these areas to bare steel, but often it is not possible to use blasting methods. Often hand cleaning is all that can be done. Careful supervision is needed, and the cleaned areas must be primed without delay and then brought forward with a suitable anti-corrosive system.

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REFERENCE

1. BS 7079:1989, *Preparation of Steel Substrates before Application of Paints and Related Products*, Part A1. Specification for Rust Grades and Preparation Grades of Uncoated Steel Substrates and of Steel Substrates after Overall Removal of Previous Coatings.

14.7 Paint Finishes for Marine Application

In considering the requirements of paints for marine use it is necessary to distinguish between the parts of ships that are subject to different conditions of service. The exterior area of ships may be divided broadly into three parts: (a) the bottom, which is continuously immersed in the sea; (b) the boot-topping or waterline area, which is immersed when the ship is loaded and exposed to the atmosphere when cargo has been discharged; and (c) the topsides and superstructure areas, which are exposed to the atmosphere but subject to spray. In addition to these weather factors, the outsides of ships are also subjected to attack arising from the conditions of use, e.g. the boot-topping is subject to abrasion by rubbing from quays, wharves and barges, while the topsides, superstructures and decks may receive mechanical damage during cargo handling. The interior surfaces, too, present varying requirements according to the conditions of use; cabins and accommodation spaces for crew and passengers call for treatment other than that demanded by cargo holds. A particular problem of ship interiors, to which special attention has been devoted in recent years, is the protection of the cargo tanks of oil and chemical tankers, and in particular those carrying acids and elemental sulphur.

Although light alloys and non-metallic materials such as reinforced plastics are finding increasing applications in shipbuilding, the principal construction material is generally mild steel. Hence the protective painting of ships is basically a special aspect of the painting of steel. In relation to atmospheric exposure, the main principles of the subject are:

- (i) Proper surface preparation.
- (ii) Appropriate composition of the paint, in particular the use of an inhibitive priming paint.
- (iii) Adequate film thickness.
- (iv) Good conditions of application.

These apply also to marine painting, but here additional factors must be taken into account. The present section refers specially to differences between ships' painting and structural steel painting.

Surface Preparation and Pretreatment

This is the most important factor determining the life of a protective paint system on steel. The best surface is one free from rust, scale, grease, dirt

and moisture, i.e. it is completely clean and dry. The removal of millscale is particularly important under marine conditions¹, especially for ships' bottoms, because the environment has a high conductivity which enables corrosion currents to pass easily between cathodic scale-covered and anodic scale-free areas. This results in pitting when the ratio of scale-covered to scale-free areas is high. A small scale-covered area with a large scale-free area is not so serious because the corrosion is spread over the larger area.

Millscale and rust can be completely removed from steel by acid pickling or by blast cleaning. Pickling was formerly used in some shipyards, but during the years 1960–65 nearly all shipbuilders installed automatic airless blast-cleaning machines for the treatment of steel plates and sections prior to fabrication. In these machines the abrasive², generally steel shot, is thrown against the steel by impeller wheels. A series of wheels directs the shot against each side of the plates as they pass through the machine at about 2 m/min, this speed being adjusted in relation to the quantity, size and velocity of the shot so that the millscale and rust are properly removed. The finish produced by these machines is normally Second Quality of BS 4232:1967 or SA2.5 of Swedish Standard S.I.S. 05 59 00–1967, and with a surface profile not exceeding 100 μm . The process is rapid and dry, and the machines are totally enclosed to prevent particles of abrasive and millscale getting into the atmosphere—accordingly they can be installed in the steel fabrication shops of modern shipyards. (Acid pickling, on the other hand, is a wet process requiring the steel to be immersed for some hours in a bath of acid and then rinsed thoroughly in water—it tended to be messy and was often banished to a corner of the shipyard.) Automatic blast cleaning of plates in these machines is much cheaper than blast cleaning after erection because labour charges are low and the abrasive is recovered, graded and re-used, fresh abrasive being added to make up for the fine particles rejected with the millscale. The cleanliness of the surface may be checked (a) visually using a hand lens, with which residual millscale and rust can be seen, (b) by the copper sulphate test³, or (c) by a reflectance method⁴. The surface profile may be checked (a) by examining the surface, or a replica, using a stylus type of surface profile instrument⁵, (b) by a simple probe type instrument⁶, or (c) by using a roughness gauge⁴ depending on the rate of leakage of gas from a cup held against the surface.

The clean, dry, slightly rough steel surface produced by blast cleaning is ideal for the application of paint, but will not remain in this state for more than a few hours under average shipyard conditions. General practice⁷ is to apply a thin coat of prefabrication primer (also known as a *blast* or *shop* primer) to the steel as it emerges from the blast-cleaning machine. The primary function of this primer is to protect the surface of the steel for the six to nine months during the fabrication and erection of the ship, but it must also meet other requirements to permit its use under practical conditions in shipyards, e.g. it must dry rapidly to permit the steel to be handled in 2–3 min, must withstand abrasion, must not affect the speed of flame cutting or welding, must not affect weld quality, must not cause any health hazards from fumes when coated steel is welded or flame-cut, and must be compatible with any type of paint system likely to be used on the different parts of ships.

The principal types of prefabrication primer in commercial use are

(a) cold-cured epoxies pigmented with zinc dust, (b) zinc silicates, (c) phenolic-reinforced wash primers pigmented with red iron oxide and (d) cold-cured epoxies pigmented with red iron oxide and inhibitive pigment. In many shipyards there are objections to the zinc types because zinc oxide fumes are evolved during welding and flame cutting, and for this reason the red oxide types are more widely accepted. The wash primer types are not universally compatible with marine paint systems, and the epoxy types are therefore recommended.

Selection of Paint Systems for Use on Ships

Exterior Surfaces above the Waterline

As indicated earlier in this section, the choice of paints for marine use depends upon the conditions of service to which the part in question will be subjected. Thus the paints used on the exteriors above the waterline and on most of the interiors do not differ fundamentally from those used on structures ashore. Inhibitive priming paints are used on steel, including those based on red lead, calcium plumbate, zinc phosphate or zinc chromate. The best known structural steel primer, i.e. red lead in linseed oil, is still used on ships, although it requires a long drying time. Slow drying is a disadvantage for marine paints, particularly on ships in service which have to be painted between voyages, since when out of commission ships are not earning any revenue. Zinc chromate primers, usually based on alkyd or phenolic media, dry more quickly than red lead in linseed oil; they are frequently used on the interiors of ships because they may be sprayed without any risk of lead poisoning and may be applied either to steel or to aluminium alloys. Lead-based priming paints should not be used on aluminium. Finishing paints are also similar to those used ashore. Good-quality alkyds are used in accommodation spaces, and the standard of workmanship is high. Colour and decorative schemes receive careful attention, and the finish is kept up to standard by frequent cleaning and regular repainting. For exterior use on topsides and superstructures, finishing paints based on alkyd media are generally used; good water resistance is essential here. White is used extensively on the superstructures of ships; owing to the pollution of many estuaries and docks with sewage and the consequent evolution of hydrogen sulphide in warm weather, it is necessary to make marine white paints 'lead-free' in order to avoid discoloration by sulphide staining. Another feature of modern marine white paints is that they are usually made from alkyds based on a 'non-yellowing' oil such as soya-bean oil in order to prevent the yellowing which occurs on exposure of linseed-oil-based white paints. The British Navy's topsides grey paint consists of rutile-type titanium dioxide in an alkyd medium based on non-yellowing oil. Black topsides paint which is used on many merchant ships may be based on phenolic media or alkyds reinforced with phenolics.

Newer types of high-performance paints⁸ used on ship exteriors include those based on epoxy resins, polyurethane resins, vinyl resins (also vinyl/alkyd or vinyl/acrylic blends) or chlorinated rubber. Epoxies and polyurethanes are chemically-curing types and present curing problems at low temperatures, whilst the overcoating intervals are critical for best adhesion

between coats. Chlorinated rubber⁹ does not suffer from these practical difficulties and is becoming widely used. A complete system based on one of these special coatings must normally be applied, and first class surface preparation is essential if the optimum performance is to be obtained from them. Simpler types of oil-based paints are generally less sensitive to the standard of surface preparation and may give better results than these special paints when imperfect surface preparation must be tolerated.

Interior Surfaces

Aluminium finishing paints are frequently used for the interior of dry-cargo holds because they help to improve lighting. Aluminium paint is also used in engine rooms; the general requirement here is for hard-drying paints resistant to oils and to heat.

Cargo and Ballast Tanks

Severe corrosion may occur in unprotected cargo and ballast tanks of oil tankers¹⁰ as a result of the combined corrosive effects of the cargoes, fresh or salt-water ballast, and tank washing by cold or hot sea-water. Ships which carry cargoes of refined oil products ('white oils') suffer general corrosion, since these cargoes do not leave any oily film on the interior surfaces of the tanks. Corrosion rates vary widely according to the conditions of service, rates of up to about 0.4 mm/y being reported. Cargoes of crude oil ('black oil') leave an oily or waxy film on tank interiors, and this has some protective action. As this film is not continuous over the whole surface, severe local corrosion may occur at areas of bare steel exposed to the action of sea-water ballast. The mechanism of the attack at these bare areas may be likened to that on small bare areas on steel which is almost completely covered with millscale; the oil or wax-covered areas function as cathodes in the same way as millscale, and corrosion is concentrated on the anodic bare areas. Some crude oils contain appreciable quantities of sulphur compounds, and residues may react with water and oxygen to produce sulphuric acid. The attack in black-oil tanks therefore takes the form of pitting; rates vary widely, up to as much as 5 mm/y being known, depending upon the conditions of service. Corrosion in oil tankers is therefore a serious problem entailing costly steel renewals in unprotected tanks. Protective measures include (a) the use of cathodic protection, (b) oxygen elimination by the injection of inert gases, (c) dehumidification of the air above oil cargoes or in tanks when empty, (d) the addition of inhibitors to the oil cargoes or to the ballast water, or the spraying of inhibitors on to the interiors of tanks, or (e) protective coatings. Methods (a)–(d) reduce the corrosion, but only (e) offers the prospect of complete protection. The coatings must have good resistance to many types of petroleum or other liquid-chemical cargoes, to ballast water and to normal tank cleaning, must not contaminate cargoes, and must be capable of being applied under shipyard conditions. Two main types of paint coating have been developed for this service, viz. epoxies and zinc silicates.

Exoxy resin paints are supplied as two components, a base and hardener, to be mixed at the time of application. Curing of the film to a tough, oil-,

chemical- and water-resistant state occurs by chemical reaction between the epoxy resin of the base component and a curing agent (amine or polyamide) forming the hardener. This reaction does not require the access of oxygen, so that the film cures right through, irrespective of thickness. It is, however, dependent on temperature, 10°C being the usual minimum practical recommendation. To ensure good intercoat adhesion, successive coats must be applied before the previous coat has fully cured, so that in practice there are maximum as well as minimum over-coating intervals, both varying with temperature. The early epoxy tank systems required application of four or even five coats to give a total dry film thickness of 200–250 μm , but common practice now is to apply two high-build coats to achieve the same film thickness. Solventless types are also available which may be applied as single coats of 200–300 μm . Coatings based on epoxy resins modified with coal tar pitch may be used in tanks for the carriage of crude oils, but are not suitable for refined oils because the pitch would contaminate the cargoes.

Zinc silicate tank coatings show good resistance to petroleum cargoes and many organic solvents, although their resistance to acids and alkalis is inferior to that of epoxies. The paints are supplied as two components, zinc dust being stirred into a silicate solution at the time of use; reactions take place during drying, the dry film consisting essentially of metallic zinc and silicic acid, together with zincates. Single coats with a thickness of 80–100 μm are normally applied.

The choice of tank coating¹¹ depends upon the cargoes to be carried, and must be determined by the ship operator with the advice of paint manufacturers. The application of epoxy or zinc silicate tank coatings demands special techniques to ensure control of surface preparation, ventilation, over-coating intervals, curing times and temperatures if satisfactory service is to be obtained, and much of the work is undertaken by contractors with the necessary knowledge and equipment. When properly applied, tank coatings not only prevent corrosion of the tanks for up to 8–10 years, but also render tank cleaning easier and quicker since cargo residues are not retained by corrosion products on the interior steel surfaces.

Ships' Bottoms

Paints used for protecting the bottoms of ships encounter conditions not met by structural steelwork. The corrosion of steel immersed in sea-water with an ample supply of dissolved oxygen proceeds by an electrochemical mechanism whereby excess hydroxyl ions are formed at the cathodic areas. Consequently, paints for use on steel immersed in sea-water ($\text{pH} \approx 8.0\text{--}8.2$) must resist alkaline conditions, i.e. media such as linseed oil which are readily saponified must not be used. In addition, the paint films should have a high electrical resistance¹² to impede the flow of corrosion currents between the metal and the water. Paints used on structural steelwork ashore do not meet these requirements. *It should be particularly noted that the well-known structural steel priming paint, i.e. red lead in linseed oil, is not suitable for use on ships' bottoms*¹³. Conventional protective paints are based on phenolic media, pitches and bitumens, but in recent years high performance paints based on the newer types of non-saponifiable resins such as epoxies,

coal tar epoxies, chlorinated rubber and vinyls have become widely used. With conventional paint systems the usual interval between drydockings is about 9 to 12 months, but with a high performance system used in conjunction with impressed-current cathodic protection, Lloyds Register and other Classification Societies permit this interval to be extended to $2\frac{1}{2}$ years.

Antifouling compositions The finishing paints on ships' bottoms are required to prevent attachment of marine growths. These paints, known as *antifouling compositions*^{14,15}, contain chemicals poisonous to the settling stages of marine plants and animals. The poisons are slowly released into the sea-water, maintaining a thin layer of water next to the surface of the paint in which the spores and larvae cannot survive; settlement and further growth are thereby prevented. The most widely used poison is cuprous oxide but its action, particularly against some types of plant growths, may be reinforced by other poisons, e.g. compounds of mercury, arsenic, tin, lead or zinc. The arsenic, tin and lead poisons are organometallic compounds. In addition, many hundreds of purely organic compounds have been examined as possible antifouling poisons, but none has yet proved so non-selectively effective against a wide range of organisms as the metallic poisons mentioned. It will be realised that antifouling compositions must have a limited effective life, because when the bulk of the poison in the film has been released, the poison release rate falls below that necessary to prevent attachment of marine organisms. On merchant ships the compositions are generally effective for about 9 to 15 months, but special long life types are effective for $2\frac{1}{2}$ –3 years.

Details of typical marine painting systems are set out in Table 14.5.

Table 14.5 Typical marine painting systems

<i>Type of paint</i>	<i>Method of application</i>	<i>Coats</i>	<i>Dry film thickness (μm)</i>
I. SHIP'S BOTTOM SYSTEMS			
<i>(a) Conventional bituminous system</i>			
Bitumen or pitch solution pigmented with aluminium flake	Airless spray, brush or roller	2–3	150–200
Antifouling composition	Airless spray, brush or roller	1	50–80
<i>(b) Conventional non-bituminous system</i>			
Tung oil/phenolic medium pigmented with basic lead sulphate, aluminium flake and extenders	Airless spray, brush or roller	2–3	150–200
Antifouling composition	Airless spray brush or roller	1	50–80
<i>(c) High performance epoxy system</i>			
Coal tar epoxy (2-pack)	Airless spray	2	200–300
Antifouling composition	Airless spray brush or roller	1	80–100
<i>(d) High performance chlorinated rubber system</i>			
Chlorinated rubber primer	Airless spray, brush or roller	1	50
High build chlorinated rubber	Airless spray	2	175–225
Antifouling composition chlorinated rubber based	Airless spray or brush	1	80–100

Table 14.5 (continued)

<i>Type of paint</i>	<i>Method of application</i>	<i>Coats</i>	<i>Dry film thickness (μm)</i>
2. TOPSIDES AND SUPERSTRUCTURE SYSTEMS			
<i>(a) Conventional system</i>			
Red lead primer in quick-drying alkyd or phenolic medium	Airless spray, brush or roller	2	100-125
Gloss finish, alkyd medium pigmented with rutile titanium dioxide (white) and tinting pigments as required	Airless spray, brush or roller	2	50-80
<i>(b) High performance epoxy system</i>			
High build epoxy (2-pack)	Airless spray	2	200-250
Gloss finish, epoxy or polyurethane (2-pack)	Airless spray or brush	1	40-60
<i>(c) High performance chlorinated rubber system</i>			
Chlorinated rubber primer	Airless spray, brush or roller	1	50
High build chlorinated rubber	Airless spray	1	80-120
Gloss finish, chlorinated rubber	Airless spray, or brush	1	50
3. INTERIOR ACCOMMODATION SYSTEMS			
<i>(a) Conventional system</i>			
Zinc phosphate primer in quick-drying alkyd or phenolic medium	Airless spray, brush or roller	2	80-100
Semi-gloss undercoat, alkyd medium pigmented with titanium dioxide and tinting pigments	Airless spray, brush or roller	1	40-60
Gloss finish, alkyd medium pigmented with titanium dioxide and tinting pigments	Airless spray, brush or roller	1	40-60
<i>(b) High performance system</i>			
Epoxy primer (2-pack)	Airless spray, brush or roller	2	100-120
Gloss finish, epoxy or polyurethane (2-pack)	Airless spray or brush	1	40-60
4. DRY CARGO HOLD SYSTEM			
Zinc chromate primer in quick-drying alkyd or phenolic medium	Airless spray, brush or roller	2	80-100
Bright aluminium finish, leafing aluminium flake in oleoresinous medium	Airless spray, brush or roller	2	50-80
5. SYSTEMS FOR CARGO/BALLAST TANKS			
<i>(a) Crude oil carriers</i>			
Coal tar epoxy (2-pack)	Airless spray	2	250-300
<i>(b) Refined oil and chemical carriers</i>			
High build epoxy (2-pack)	Airless spray	2	250-300

Note: The above systems are for application to steel blast-cleaned to a 'near-white' finish (Second Quality of BS 4232:1967) and immediately shop-primed before fabrication. The shop primer must be thoroughly cleaned and degreased at the time of painting.

Methods of Application (Section 14.1)

The paints used on ships may be applied by brush, roller or spray—airless spraying in particular being widely used when large areas are to be coated. High performance coatings are formulated to permit application of the full system in only a few coats, i.e. the paints must be capable of airless spray application at wet film thicknesses of 200–500 μm without sagging or running on vertical surfaces, to give dry film thicknesses of 100–300 μm per coat. Time in drydock is generally restricted owing to high costs—figures of £20 000–£40 000 per day being quoted for a 20 000 t tanker—so ships' paints must dry rapidly and must tolerate application under non-ideal weather conditions since owners are unwilling to incur extra costs from delays in painting. Possible health hazards, particularly when spraying some types of antifouling compositions, must be guarded against by wearing protective masks and equipment.

Economics

In the painting of the general interior spaces and the exterior surfaces of ships above the waterline, protective and decorative aspects cannot be separated. Thus, on passenger liners the frequency of repainting the accommodation, superstructure and topsides is determined primarily by the decorative appearance, while on cargo ships this is usually less important than protection. For ships' bottoms the maintenance of a smooth surface free from marine fouling growths is important because a rough or fouled bottom leads to reduced speed and/or increased fuel consumption. Fouling may easily cause a 50% increase in fuel consumption, involving an appreciable increase in running costs. For this reason the intervals at which ships' bottoms are repainted depend on the efficiency of the antifouling compositions and on the degree of fouling encountered in service, marine growth being more vigorous in warm tropical seas than in temperate or polar waters.

The cargo tanks of oil tankers present a special case, because of the high cost of steel renewals in unprotected tanks. For a 30 000 t tanker, costs in the region of £500 000 for the initial painting of the tanks have been quoted; if the life of the paint system is 6–8 years, the total cost over the normal 20-year life of a tanker is expected to be appreciably less than the sum otherwise spent on steel renewals, which may amount to several hundred thousand pounds.

Types of Failure (Section 14.4)

Paints correctly applied to well-prepared surfaces on the above-water part of ships will normally fail first by chalking, with checking and crazing of the finishing paint following. Of the high performance systems, polyurethanes have better gloss retention than epoxies or chlorinated rubbers. In spite of a general improvement in conditions of application during recent years, however, ships' paints are still liable to be applied to damp or otherwise imperfectly prepared surfaces, and this leads to failure by adhesion

breakdown and rust formation beneath the paint film. Intercoat adhesion failure is also likely with epoxy systems if recommended intervals between coats are exceeded.

On ships' bottoms the antifouling coat fails when its poison release rate (or leaching rate) falls below the value needed to prevent attachment and growth of marine fouling organisms. At this stage it becomes necessary to drydock the ship, clean the bottom and re-apply antifouling composition; the underlying protective paint system should normally only need renewal after about four or more years, depending on whether a conventional or a high performance system is used. For economic reasons (docking charges, interest, insurance, loss of earnings, etc.) no delay can be accepted in the repainting of ships' bottoms, so painting sometimes proceeds under adverse weather conditions to a poorly prepared surface—in consequence failure may occur from loss of adhesion. Paints capable of application to damp surfaces are being developed to overcome this difficulty. It may also be mentioned that promising results have been obtained by cleaning and recoating ships' bottoms under water, and this could eventually eliminate drydocking of ships for repainting^{16, 17}.

Recent Developments

During the years since the publication of the second edition there have not been any really fundamental changes in the materials and methods of painting ships, although there have been changes to meet differing application and health requirements and to take advantage of technical developments. Improved quality control has also led to better corrosion protection. The British Ship Research Association¹⁸ and the Dutch Paint Research Institute TNO¹⁹ have published ship painting manuals; reviews of marine paint technology have been published by De la Court and de Vries²⁰, Phillip²¹ and Banfield^{22, 23}.

In this section changes are described under the original headings, but some of the figures in Table 14.5 and in the subsections 'Methods of Application' and 'Economics' have also been updated.

Surface Preparation and Pretreatment

Blast-cleaning in impeller-type machines is now almost universally used for the initial surface preparation of ships' plate²⁴, earlier methods by weathering, scraping and wirebrushing or by acid pickling being practically unknown in modern shipyards. The design and performance of the machines have been improved. More attention is given to the selection of suitable grades of abrasive, its recovery and grading before reuse to ensure that the most suitable balance of coarse, medium and fine particles is actually used. In addition to surface cleanliness the surface profile of the blast-cleaned surface is now frequently specified—this has a considerable bearing on the adhesion and performance of priming paints.

The prefabrication primers previously described are still current, the phenolic-reinforced wash primers being most widely used for general ship

construction. For cargo tanks designed to carry chemicals or solvents it is preferable to apply the epoxy tank coating direct to a freshly blast-cleaned surface because small amounts of some cargoes can become absorbed into the coating and soften a polyvinyl butyral primer, leading to adhesion failure.

Exterior Surfaces above the Waterline

The use of oleoresinous paints has declined, being confined to smaller ships—practically all large ships use high performance coatings. Priming paints containing lead pigments are hardly ever used because of a greater awareness of possible health hazards. Similarly, the use of zinc chromate primers is declining because soluble chromates are believed to be carcinogenic; this has led to the increased use of zinc phosphate primers.

As stated above, high performance coatings based on epoxies, vinyls or chlorinated rubbers are used almost exclusively on all large ships. A general development in these materials has been the introduction of highly thixotropic²⁵ types that can be airless sprayed at wet film thicknesses of 300 μm or more, that do not run or sag on vertical surfaces. This enables the requisite film thickness to be applied in fewer coats, saving time and reducing application costs.

Cargo and Ballast Tanks

The zinc silicate, epoxy and coal tar/epoxy coatings are still used. Coal tar epoxies are used for crude oil tanks, sometimes on all the interior surfaces but more often for (a) the bottom of the tank and about 2 m up the sides, (b) the top of the tank and about 2 m down the sides, and (c) other horizontal surfaces where seawater ballast may lie. These partly coated tanks are frequently also fitted with cathodic protection to prevent corrosion of the uncoated areas when seawater ballast is carried. The pure epoxy or coal tar epoxy coatings applied in bulk cargo tanks used for the carriage of grain must be approved by the North of England Industrial Health Service, or by similar independent authorities in other countries.

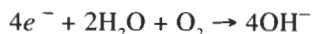
In the case of some tanks used to carry wine or chlorinated solvents the final coat applied over an epoxy coating is sometimes an oil-free polyurethane enamel because this paint resists chlorinated solvents better than do epoxies, does not taint wines and is not stained by red wines.

Ships' Bottoms

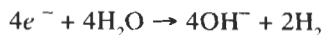
The conventional bituminous or oleoresinous paints previously described are still used on the bottoms of smaller ships, the chief difference being that they are applied mainly by airless spraying. The formulations may be adjusted to permit application of thicker coats than by brush or roller, although the coats must not be too thick because oleoresinous paints require

access of atmospheric oxygen to permit drying—very thick coats would take an impractically long time to become dry.

The outer hulls of large ships are protected by one or other of the high performance systems previously described—epoxies, vinyls or chlorinated rubbers, often blended with coal tar. Here, too, as already described for surfaces above the waterline, highly thixotropic types have been introduced permitting the required film thickness to be applied in fewer coats, saving time and reducing application costs. These large vessels are almost all fitted with cathodic protection²⁶ using an impressed current system in which inert anodes (e.g. platinised titanium, lead alloy) fitted on the hull are energised by a low voltage d.c. generator. This causes the entire surface of the hull to become a cathode at which electrons are discharged; in the presence of an ample supply of oxygen the reaction is:



The high performance coatings mentioned are all non-saponifiable types, so resist the alkaline conditions on the hull. In the vicinity of the anodes the current density is inevitably higher than elsewhere on the hull and the rate of production of hydroxyl ions is correspondingly higher, i.e. conditions become highly alkaline. This leads to the deposition of calcium and magnesium carbonates ('cathodic chalk') near the anodes. Another effect of the high current density is that dissolved oxygen in pores in the coating becomes exhausted and the cathodic reaction then becomes:



with evolution of gaseous hydrogen. These two effects both tend to disrupt the coatings. They are minimised by (a) electronic control of the cathodic protection installation to ensure that the hull potential is no more than required for protection, and (b) surrounding the anodes with rubber mats or glass reinforced plastic shields.

Antifouling Compositions

Until recent years these paints could be classified²⁷ broadly into two groups. In *soluble matrix* antifouling paints the particles of poisonous pigments (chiefly cuprous oxide) are distributed throughout the film of a resin-based binder which dissolves slowly in seawater. Dissolution of the binder exposes the particles to the action of the seawater, thus maintaining a thin layer of water next to the hull which is poisonous to the spores and larvae of marine plants and animals. In *contact* antifouling paints the poison content is high enough to ensure that particles of poisonous pigment (chiefly cuprous oxide) are in contact throughout the film. As the particles near the surface dissolve other particles deeper in the film become exposed to the action of the seawater, thus maintaining a toxic layer of water next to the hull.

In more recent years two new types of antifouling composition have been developed, using organometallic compounds as poisons. In one type²⁸, based chiefly on vinyl resin and organotin compounds (e.g. tributyltin fluoride), the poison and resin form a solid solution. As the poison dissolves from the surface of the film, more poison diffuses from deeper in the film to

maintain a uniform concentration throughout the film, i.e. the poison released to the seawater is replenished by diffusion from within the film. This mechanism hardly disturbs the surface of the paint which therefore retains its original smoothness. The other new type²⁹ is based on a toxic component combined with a binder resin, e.g. tributyltin acrylate may be copolymerised with an acrylic resin, producing a film-forming copolymer resin with a high content of tributyltin groups. When applied as a paint to a ship's bottom the polymer is slowly hydrolysed and toxic tributyltin groups released into the seawater. The residue of the polymer is water soluble. In this way the surface of the film is slowly eroded and the action is claimed to maintain a smooth finish on ships' bottoms. Since 1986, however, an account of ecological and pollution problems associated with organotin compounds, and allied Health and Safety Regulations, the use of these compounds in antifouling compositions has markedly declined³⁰.

Reference is made in the foregoing paragraph to the smoothness of ships' bottoms, and the importance of this factor has become increasingly realised in recent years. A rough surface, whether caused by attachment of fouling organisms, by corrosion or by poor paint application techniques, leads to an appreciable increase in the resistance to movement of a ship and hence to increased fuel consumption to maintain the service speed. The British Ship Research Association¹⁸ has developed a gauge to measure hull roughness, and this is used to check that the surface of the underwater hull of new ships is satisfactorily smooth—similar measurements are made after cleaning and repainting in service.

Methods of Application

Reference has already been made to the greatly increased use of airless spraying for applying paints to ships. On the largest vessels the use of brushes or rollers is impracticable: the area of the outer hull of a 300 000 t tanker exceeds 30 000 m². Thus, high-build coatings cannot satisfactorily be applied by brush or roller—eight or ten coats would be needed, requiring many painters and a long time. One airless spray gun, however, is capable, under practical conditions, of applying thick coats at up to 400 m²/h. Four or six guns, therefore, will apply one coat to the entire area in a few days and the complete paint system in under 2 weeks.

Airless spraying produces less spray mist than conventional air-assisted spraying, but there is some risk of inhalation of spray droplets by painters or by others working in the vicinity. The danger may be avoided by wearing a filter type face mask. When applying³¹ antifouling compositions suitable protective equipment must be worn because of the poisonous compounds they contain—this applies particularly to some of the newer types containing organometallic compounds but also to the older types containing cuprous oxide.

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14.8 Protective Coatings for Underground Use

Introduction

The general conception of a paint is of a cold-applied material containing thinners which evaporate to leave a higher molecular-weight base protective, of 25–50 μm thickness per coat. For buried or submerged structures, where maintenance is difficult or even impossible and a degree of physical protection is also necessary, such thin protective paint barriers between metal and the corrosive electrolyte environments of soil or water are usually quite inadequate. In relatively non-corrosive soil, thin bituminous coatings on thick cast iron may be satisfactory, but this is the exception rather than the rule. In dealing with underground structures, therefore, the thicker protectives needed are regarded as *coatings* rather than as paint finishes.

The most usual forms of buried metal structures are pipelines, piles, tanks and power and telephone cables. Power cables must usually have some metal protection, covered by expensive continuous factory-applied sheathings of considerable thickness. Since water, gas and petroleum pipelines provide the greatest area of metal surfaces to be protected below ground, a detailed discussion of the protection given to them would appear to be the best means of dealing with coatings for underground use.

Improvements are continually being made in the quality of coating materials and their application, but it is still difficult to produce at economic cost a permanent coating for a buried pipeline. The disruptive effects of handling, construction, penetration by rocks, soil stress, material ageing, etc. inevitably result in areas of bare metal being exposed to corrosive soil electrolyte at isolated locations, with ultimate pitting or holing of the metal. The aim is to supply the best possible coating at economic cost and to provide for any initial or later failures by application of cathodic protection. The combination of coating with cathodic protection shows the greatest economic advantage.

In pipelining, the trend is towards all-welded steel for long lines, and since the wall thickness is less than that of cast iron, protection is the more important. Many types of coating are used, from thick concrete to thin paint films, and each has its own particular suitability, but the majority of pipelines throughout the world today are coated with hot-applied coal tar or petroleum asphalt-base-filled pipeline enamels, into which reinforcing wraps, such as glass fibre are applied.

The use of coatings applied in the form of tape is also increasing. Polyethylene and polyvinyl chloride films, either self adhesive or else supporting films of butyl adhesive, petrolatum or butyl mastic are in use as materials applied 'cold' at ambient temperatures. Woven glass fibre or nylon bandage is also used to support films of filled asphalt or coal tar and these are softened by propane gas torches and applied to the steel surface hot, cooling to form a thick conforming adherent layer.

Recently, sheets of high density polyethylene extruded on to the pipe surface over an adhesive have become available and the use of polyethylene or epoxy powders sintered on to the steel surface is becoming more frequent.

Some use has been made in the water industry of loose envelopes of polyethylene sheeting and with the increasing lengths of submarine pipeline requiring heavy concrete coatings for reducing buoyancy, the use of a heavily filled bituminous coating is projected.

In the special case of pipelines operating at relatively high temperatures such as for the transmission of heavy fuel oil at up to 85°C, heat insulation and electrical insulation are provided by up to 50 mm of foam-expanded polyurethane. As a further insurance against penetration of water, and to prevent mechanical damage, outer coatings of polyethylene (5 mm), butyl laminate tape (0.8 mm) or coal-tar enamel reinforced with glass fibre (2.5 mm) have been used.

Properties Required of Buried Coatings

The aim in applying a coating to a buried metal such as a pipeline is to prevent electrical contact with an electrolyte such as soil and/or water. The characteristics required are as follows:

1. *Ease of application.* It must be possible to apply the coating in the factory or in the field at a reasonable rate and to handle the pipe reasonably quickly after the coating has been applied without damaging the coating.
2. *Good adhesion to the metal.* The coating must have an excellent bond to steel. Priming systems are frequently used to assist adhesion.
3. *Resistance to impact.* The coating must be able to resist impacts without cracking.
4. *Flexibility.* The coating must be flexible enough to withstand such deformation as occurs in bending, testing or laying, as well as any expansion or contraction due to changes in temperature. It must not develop cracks during cooling after application or curing.
5. *Resistance to soil stress.* The coatings are often subject to very high stresses, due, for instance, to the contraction of clay soil in dry weather, and they must be able to resist such stresses without damage.
6. *Resistance to flow.* The coating should show no tendency to flow from the pipe under prevailing climatic conditions. It must not melt or sag in the sun and it must have sufficient resistance not to be displaced from the underside of large-diameter pipes.
7. *Water resistance.* Coatings must show a negligible absorption of water and must be highly impermeable to water or water-vapour transmission.

8. *High electrical resistance.* The coating must be an electrical insulator and must not contain any conducting material.
9. *Chemical and physical stability.* The coating must not develop ageing effects, e.g. denaturing due to absorption of the lower-molecular-weight constituents, or hardening with resultant cracking from any cause including oxidation. It should be stable at operating temperatures.
10. *Resistance to bacteria.* The coating must be resistant to the action of soil bacteria.
11. *Resistance to marine organisms.* In the case of submarine lines, the coating should not be easily penetrated by marine life, e.g. mussels, borers, barnacles, etc.

These characteristics cover the general ideal for a pipeline coating, but obviously modified conditions may impose requirements which are more, or less stringent; this of course also applies to other types of buried structures.

Preparation of Metal Surface

Before applying a protective coating it is essential to ensure that the surface is free from rust, millscale, moisture, loose dust, or any other incompatible material which might prevent the electrically non-conducting coating from bonding properly with the metal surface or which might produce defects in the continuous film.

The following cleaning methods are available and each may have a particular advantage in given circumstances:

- (a) *Mechanical cleaning.* Hand or mechanical wire brushing, impacting or abrading are methods suitable for hot applied coatings, for repairs to damaged areas or for relatively small or inaccessible areas. Visual standards to assess the degree of cleanliness are available but are not commonly used.
- (b) *Blast cleaning.* Air-blast or centrifugally-impacted sand, shot or grit are appropriate for thin-film multicoat systems or for continuous factory production. Several visual standards are available. The cost of attaining a very high standard of cleanliness is considerable, and careful consideration should always be given to specifying the correct level of blasting for the particular application.
- (c) *Pickling.* Dipping in inhibited hydrochloric or sulphuric acid is commonly used in factory production, particularly in conjunction with hot phosphoric acid dipping (Footner process). The considerable facilities necessary for this method limit its use to the larger steel producers. Published standards are available for the phosphate surface conversion coating process.
- (d) *Flame cleaning.* This is appropriate only for field repair work where a dry or warm surface can be obtained only by flame application and must be preceded usually by mechanical cleaning.
- (e) *Pipeline travelling machine.* For long runs on continuously-welded pipelines, a machine with rotary wire brushes and/or impact tools and cutting knives may be used to prepare the surface. These machines,

which are self-propelled along the pipe itself, are commonly combined with drip or spray apparatus to apply the primer which is spread over the surface by rags or brushes so that the prepared surface is immediately primed.

No matter which method of cleaning is adopted, it is desirable to apply the primer or coating immediately after the cleaning operation.

The preparation of the metal surface to receive the protective coating is of prime importance since a coating which is not bonded to the metal surface can allow electrolytes to contact the metal, with resultant corrosion. If water films develop between the metal and the electrically non-conductive coating, cathodic protection becomes ineffective.

Coating Techniques (Section 14.1)

Dipping, Spraying and Brushing

These methods are generally appropriate for either thin-film solvent-based paints or for coatings up to about 150 μm thickness. The techniques are more usually used for the priming layer of the coating systems.

Factory or Yard Application

Protective coatings applied at a factory have the advantage that the work can be carried out under strictly controlled conditions but suffer from the disadvantage that they may be damaged during transport to the site.

Pipes are frequently shot-blasted or descaled by acid pickling, then phosphated, either sprayed with primer or dipped into a bath of hot asphalt to provide a thin prime coat. The dry primed pipes are then slowly rotated by a lathe head, while hot enamel, mastic or asphalt/micro-asbestos paste is applied from a hopper travelling alongside the pipe. A pipe coating approximately 5 mm thick is produced by use of a heated pallet attached to the hopper feed. Reinforced-glass wrapping materials may also be spirally wound on to the coating according to requirements.

'Rolling Rig, 'Fixed-head' and 'Rotating-head' Coating Machines

The coating equipment under this heading may be used in permanent factories, but is often set up at temporary coating yards close to the location where the pipes are to be laid. The coating produced is usually 2–3 mm per pass.

Rolling rig machines The rolling rig machine rotates the cleaned and primed pipe on mechanically driven 'dollies', while a tank travelling alongside the pipe floods it with hot asphalt or coal-tar-base enamel.

At the same time internal and external reinforcing wraps may be spirally wound into or on to the hot enamel.

Fixed-head machines Fixed-head machines are fed with the cleaned and primed pipe, which mechanically rotates as it passes through the fixed coating head which floods the hot enamel on to the pipe. At the same time reinforcing wraps are pulled on to the rotating pipe.

Rotating-head machines In rotating-head machines the coating head and wrapping spindles rotate as the pipe is fed through the machine.

Pipeline Travelling Machines

In the case of long continuously-welded steel pipelines the above pipe-coating methods present the disadvantage that the joints have to be coated in the field after welding. To overcome this difficulty equipment which travels along the welded pipeline has been developed.

A mechanically propelled cleaning machine travels along welded lengths of the pipeline. The machine has counter-rotating cutting knives or brushes, and also applies by rotating swabs, a thin coating (cold application) of primer to the clean metal surface. When the primer is dry, a coating and wrapping machine travels along the pipeline.

The wrapping materials usually consist of staple glass tissue, pulled half-way into the hot enamel, and an outer wrap of glass impregnated with coal-tar or asphalt enamel to produce a coating of approximately 2-5 mm as shown in Fig. 14.5.

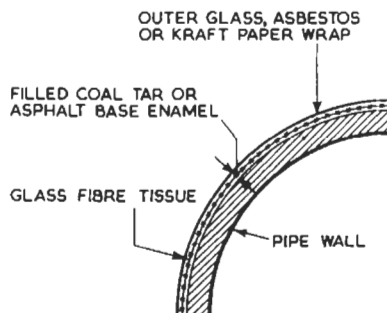


Fig. 14.5 Type of coating produced by mechanical flood coat and wrap machine

These machines can coat and wrap up to 5 km of pipeline per day. After the coating has been checked for pin holes by a high-voltage rolling-spring electrode, the pipe may be lowered directly into the trench, so that undue handling is avoided. The line travelling machine is usually used with coal tar or asphalt-base pipeline enamels. Similar line travelling machines are in use for the cold application of tape coatings.

Types of Coating Materials (Section 14.2)

Plasticised Coal Tar and Petroleum Asphalt Enamels

The majority of pipelines today are coated with hot-applied plasticised coal tar or petroleum asphalt enamels. Both coal-tar pitch and petroleum asphalt have been used as protectives with and without filling materials. When filled

they are termed *enamels* or *mastics*. The term *bitumen* or *bituminous* has always been loosely applied and it is preferable to specify petroleum asphalt base or coal-tar pitch base.

Straight and filled enamels Fillers are normally added up to a maximum of about 30% weight (calculated on the mixture) which is equivalent to about 15 to 20% by volume. A filled coal-tar pitch has a higher softening temperature (as shown by the 'ring and ball' test) than the unfilled material, which results in a reduced tendency to flow. This fact is important in tropical countries or if a pipe is to operate at a somewhat elevated temperature. Resistance to impact and abrasion of a coating is improved by the filler. The viscosity of the pipe coating is also increased; this entails a higher application temperature (193–249°C).

A satisfactory filler must have the following characteristics:

1. Low water absorption. In this respect certain fine clays are unsuitable.
2. Ability to be readily wetted by the enamel.
3. Finely-ground composition, particles preferably of laminar shape to prevent settling when the enamel is molten.
4. Relatively low specific gravity, so that there is the minimum tendency for the filler to settle-out in the melting kettle.

In present-day practice the materials which are commonly used and which satisfy most closely these requirements are talc, pumice powder, micro-asbestos and slate powders.

It must be appreciated that there is an optimum percentage of filler which imparts to a coating the required melting point and toughness; beyond this point application becomes more difficult and watertightness may be impaired.

Petroleum asphalt or coal-tar pitch as coatings The question of whether coal-tar pitch or petroleum asphalt is the more suitable for the coating of underground pipelines has raised a good deal of controversy. Asphalt and pitch are both waterproof materials, and they resemble one another in physical type. In the right circumstances both can be very effective in preventing the access of water to buried or submerged steel surfaces.

Petroleum asphalts are manufactured in two general types: (a) a straight residue from distillation, which can be of the hard, high-melting type, and (b) so-called 'blown' grades which are prepared by partially oxidising the asphalt base by blowing in air. The general difference between the two grades is that 'blown' asphalt has a higher softening point than straight asphalt of the same penetration (i.e. hardness). In assessing a pipeline coating the softening point is of considerable importance, since it determines the tendency to flow, and a certain minimum softening point is therefore necessary. A 'blown' asphalt has the advantage over straight material of the same softening point in that it has a better resistance to impact, since it is of a more rubbery nature. For this reason most petroleum asphalt coatings are based on the 'blown' variety.

So far as coal tar is concerned, it was formerly the custom to use the straight residual pitch, but nowadays shock resistance is improved by a so-called plasticising process.

The differences between asphalt and coal tar in relation to their application as pipeline coatings require comment.

1. It is often claimed that a coal-tar-base coating absorbs less water than an asphalt coating and there is evidence in practice to support this claim, but some asphalt enamels in practice have been as good as the best coal-tar enamels.
2. Coal-tar enamels are claimed to have better adherence than the asphaltic enamels to clean metal, probably because of the presence of polar compounds, but little difference can be noted in practice under proper pipelining conditions.
3. The asphaltic enamels are easier to apply since they do not produce so much obnoxious fume and are usually applied at slightly lower temperatures.

The field performance of the asphalt-base pipeline enamels was, at one time, erratic, probably because the material had been drawn from varying sources, without a close specification being used. The plasticised coal-tar-base enamel to the American Water Works Association Specification C-203 thus gained some favour in major pipelining organisations.

The AWWA C-203 Standard remains a widely used specification suitable not only for the materials, but also for their associated reinforcing wraps and application procedures. The standard has been regularly updated. Hot-applied asphaltic and coal-tar coatings with their priming systems are now well classified, described and specified in BS 4164:1967 (coal tar) and BS 4147:1967 (asphalt), but no guidance is given in these specifications to application procedures.

Reinforcing materials

Internal At one time open-weave hessian cloth was very largely used as an internal reinforcement material, but experience showed that this is subject to rotting in the soil. Even when the material appears to be covered with enamel, some of the fibres must protrude, and thus moisture is absorbed so that after a period of years the hessian is generally found to be in a water-logged condition and forming food for bacteria.

The type of material to be used depends very largely on whether coating is carried out mechanically or by hand. For hand application it is not possible to use comparatively fragile staple tissues made of glass or asbestos and it is necessary to use a strong open-mesh fabric, such as woven asbestos or woven glass. The woven wraps are a great deal more expensive than the staple tissues, which are mechanically applied.

It is not economical to use expensive woven material for long lines, which can be, and normally are, coated by mechanical means. For such lines the most commonly used material nowadays is a glass-fibre tissue of a nominal 0.5 mm thickness, consisting of glass fibres bonded together with a phenolic resin or starch.

The improvement in coating quality achieved by using the internal glass wrap is illustrated by the following results. The tensile strength of a 3.2 mm thickness of 104°C softening-point enamel, 300 mm × 300 mm is virtually nil. A piece of 300 mm × 300 mm glass tissue 0.5 mm in thickness will break at about 50 kg under steadily increasing tensile load, but if it is embedded

in 3.2 mm of the enamel a tensile strength of the order of 150 kg is obtainable. These wraps are now longitudinally reinforced to prevent tearing on line-travelling or other coating machines.

Where the pipeline is expected to have to withstand unusual dimensional variation due, perhaps, to temperature changes or near yield point pressure testing, the use of a woven glass or nylon reinforcement in place of the glass tissue is said to increase the flexibility of the coating system considerably.

External wrap The purpose of an external overlapping wrap is to provide a shield against the penetration of the enamel by stones and to prevent the pulling of the enamel away from the pipe by soil stress. It also reduces flow of the enamel owing to the weight of the pipe, and damage to the coating caused by handling can be more easily observed.

The properties required of an external wrap are as follows:

- (a) Compatibility of impregnant to bond with the enamel used.
- (b) Tensile strength to prevent breaking while wrapping.
- (c) Hardness to resist penetration.
- (d) Flexibility to allow wrapping without cracking.
- (e) Free rolling from the reel while wrapping.
- (f) Resistance to soil conditions and bacterial attack.
- (g) Non-absorption or low absorption of water.

These properties apply to a reinforcing outer wrap such as coal tar or asphalt-impregnated glass or asbestos bonded lightly to the outside of the hot-applied enamel. For some conditions kraft paper is adequate to facilitate handling and reduce soil stress. Were it not for its screening effect on cathodic protection with a consequent decrease in the effectiveness of the latter, the external wrap could be loose around the coating. It has become conventional to have the external wrapping lightly bonded to the coating to prevent lamination and water entry.

Armour wrapping In rocky ground it has always been considered good practice to pad the trench for a buried pipeline with clean sand. This procedure can be very expensive if the sand has to be hauled long distances, and an armour wrap has been developed to supplement the normal outer wrap to meet such conditions.

A typical wrap is supplied in sheets about 6 mm thick, consisting of a sandwich of mastic enamel between sheets of asbestos about 1.5 mm thick. It may be longitudinally indented to allow the material to be wrapped around the pipe and secured by steel ribbon straps.

An objection to this form of wrap is that its mode of application renders it extremely difficult to obtain a good uniform bond between the wrap and the enamel. In view of this, water could become trapped under the armour wrap, and because of the non-conducting nature of the wrap itself the effective application of cathodic protection would be difficult.

Cold-applied Tapes

Hot-applied coatings require special melting and handling equipment to be available at the construction site. Clearly, considerable economies are possible if this equipment can be dispensed with, particularly in remote areas

with difficult access. Thus, the availability of cold-applied tapes for use either at the joints between factory-coated pipes or continuously over the pipeline has led to the increased usage of this type of wrapping.

The tapes are usually relatively thin (0.5 mm) and easily damaged. It is, therefore, essential to take elaborate precautions to provide physical protection to the tape once it has been applied both during construction and after burial. Good results have been obtained when the tape is applied by line travelling machine and without further handling, immediately lowered into a sand padded trench and covered over with fine sand before the trench is back filled.

Initial effective electrical resistance of tapes, as evidenced by the cathodic protection current demand, has been outstanding. There have been reports of increasing current demand with time which indicate a need for investigation. The current demand increase has been found, on occasion, to be due to poor construction practice, but not all tapes are affected in this way.

On large diameter pipes having a raised seam weld, difficulty is encountered in covering the weld 'shadow' effectively.

Petrolatum-type tapes Petrolatum has, like lanolin, long been recognised as a means of preventing corrosion. It is easily cold-applied and has a definite place in corrosion engineering, but it is not suitable for buried structures, unless it is screened from soil and water by a woven glass or nylon cloth or an impervious membrane such as p.v.c. The polythenes normally tend to swell in contact with it. Earlier petrolatum coatings were frequently applied with cellulosic backing material; there were several objections to this type of protection, e.g. attack by sulphate-reducing bacteria on the cellulose, absorption of the grease by dry bentonite-type clays, lack of physical strength against stones, and water absorption.

Petrolatum-type tape coatings now incorporate inhibitors against bacteria and with their backing film have high electrical and water resistance and therefore find extensive applications in the UK. A great advantage of the petrolatum-type coatings is ease of application and conformability to irregular surfaces.

Pressure-sensitive tapes Unlike the more recently developed petrolatum tapes which rely on both the petroleum and backing films, the pressure-sensitive tapes offer protection which depends almost entirely upon the prevention of ingress of moisture to the metal surface by the tape itself.

The tapes are cold-applied, either by hand or by mechanically-operated equipment moving along the cleaned pipeline.

The tapes are usually produced from polythene or polyvinylchloride films of 25 μ m to 0.5 mm in thickness and the inner surface is coated with an adhesive, frequently rubber-based. The adhesive is usually between 25 and 100 μ m thick.

Earlier tapes frequently suffered from the migration of plasticiser from the tape to the adhesive with the result that the tape became detached from the metal, to which the adhesive remained attached. This has now been overcome by using a barrier between the tape and adhesive which itself may contain inhibitors against soil bacteria.

Spiral corrosion due to inadequate overlap has been detected with self-adhesive tapes, and a 25 mm (or preferably half-tape-width) overlap is to be advocated. Within normal limits, the thicker the adhesive the better.

The self-adhesive tape coatings are thin and the adhesive itself does not necessarily come into contact with the valleys in the cleaned metal surface. Under these circumstances, the transmission of water vapour through the film to the metal may be possible. Moisture-transmission characteristics and other properties of p.v.c. and polyethylene tapes, as given by major manufacturers, are provided in Table 14.6.

Table 14.6 P.V.C. and polyethylene tapes

<i>Material</i>	<i>Physical property</i>					
	<i>Thickness of film plus adhesive (mm)</i>	<i>Tensile strength (kg/cm width)</i>	<i>Elongation at break (%)</i>	<i>Moisture absorption (%)</i>	<i>Moisture-vapour transmission rate (g/m² per 24 h)</i>	<i>Dielectric strength (V)</i>
P.V.C.	0.229 + 0.025	10	175	0.19	24.0	10 000
Polyethylene	0.203 + 0.100	10	70	0.02	3.1	14 000

Table 14.6 is only indicative of general properties, and the latest developments of specific manufacturers of self-adhesive tapes may show advances on these.

P.V.C. tends to be more conformable to irregularities than polyethylene. Both types have their right and proper application for buried structures.

Laminated tapes In more general use now than pressure sensitive tapes are tapes consisting of polyvinyl chloride or polyethylene films in conjunction with butyl rubber. These tapes are applied with an adhesive butyl rubber primer. Thicknesses of up to 0.75 mm are in use and loose protective outer wraps of p.v.c. or polyethylene sheet are commonly applied. Tape quality control is exercised with reference to ASTM standard test methods and may include water vapour transmission rate and elongation.

Conventional holiday-detection is of little value in the field but great attention should be given to preventing damage to the applied tapes.

Coal-tar Epoxy Coatings

The epoxy resins when mixed with the correct amine produce tough films which adhere closely to metal. The chemistry of these resins is considered in Sections 14.5 and 14.9.

The thickness and water resistance of the normal air-cured film can now be much improved by the incorporation of suitable coal-tar pitch material. A typical coal tar/epoxy coating material would be constituted as follows:

Epoxy resin	30
Coal-tar pitch	25
Filler	25
Solvent	20

and to the above would be added the amine curing mix.

The coating is of the two-pack type, consisting of resin plus curing hardener. In practice the resin and amine may be mixed together and used for application by brush or spray, or by mechanical means at ambient temperature. Sometimes the clean metal is heated, as are the coating components which are then sprayed separately on to the metal to reduce curing time. Little reaction occurs below 4°C. For pipeline coating the pipes can usually only be handled after a few hours, depending on the mix and temperature, but it takes anything from two to seven days before the best characteristics of the coating develop.

Information to date indicates that the total thickness of the coating should not be less than 0.3 mm and this requires several applications. These coatings are very tough and closely adherent (one pipeline company states that they handle coal tar/epoxy-coated pipe like bare pipe, including bending in the field). The first coal tar/epoxy coatings came into use only in 1953, and although they seemed most promising they have been little used to date compared to other materials. This is undoubtedly due to their relatively slow setting and curing time.

Polyethylene Sheet

The practice has been developed amongst some water undertakings to envelop uncoated spun iron pipes in 0.5 mm thick polyethylene sheet, the ends of which are tied down to the pipe with a substantial overlap by means of adhesive tape. This method has great advantages in cost and simplicity. No long term performance figures have been published but many have grave doubts about the effectiveness of this method since the possibility of aggressive soil water entering at perforations or through overlaps, appears to be very high.

Foam Polyurethane

These materials have been finding extensive use on transmission pipelines supplying heated heavy fuel oils to power stations. To prevent damage to the 50 mm thick coating, a mechanically stronger outer wrap which can also prevent water ingress is usually necessary. In one method of production, the foam is manufactured inside a polythene tube over the steel tube. In other methods where the foam is produced by spraying on to the steel surface, conventional tape or enamel coatings have been used.

Weight Coatings

For pipelines to be placed under water, it is necessary to provide negative buoyancy. This is commonly achieved by placing lightly reinforced concrete up to 150 mm thick over the 3–5 mm hot enamel coating on the steel. Joints at the welded tube ends have to be coated with a minimum of delay due to the high production rate required on the laying barge, and tapes have therefore found application at this point. Where submarine pipelines are 'pulled'

into position off the land, joint repair is more commonly carried out by means of the same hot enamel used as the pipeline coating. For the final joint between towed 'strings' of up to 300 m, fast setting epoxies have been used.

A composite asphaltic mastic filled with high-density aggregate is now available as a combined insulation and weight coating, and this could be the development area in this field.

Internal Pipeline Coatings

In some instances it is necessary to coat pipelines internally, and materials widely used are red lead, hot-applied enamels, concrete and epoxy resins.

Internal coatings are usually applied at the factory and no difficulty exists in field construction if flanges, screwed, or spigot and socket joints are used, nor is there any difficulty with welded pipes above, say, 750 mm diameter, where patching can be carried out on the joints from the inside. Repair of internal coating on smaller-bore welded pipes presents many problems, which have not yet been satisfactorily overcome for all conditions.

Pipelines in the ground can be mortar lined *in situ* by the use of travelling devices. Epoxy resin paints for long welded pipelines already laid have been applied *in situ* by placing two plugs in the pipeline with the paint between them, and then forcing them to travel through the pipeline by the use of compressed air.

Recent Developments

Recent trends in protective coatings used on buried pipelines have been away from reinforced hot applied coal tar and asphalt enamels and butyl rubber laminate tapes, particularly where applied 'over-the-ditch'. The more recently developed coatings based on fusion bonded epoxies, extruded polyethylenes, liquid-applied epoxies and polyurethanes, require factory application where superior levels of pipe preparation and quality control of the application process can be achieved.

The longest most successful track record is still claimed by reinforced hot enamels, with their performance beneath concrete weight-coating making them first choice for the majority of North Sea offshore pipelines installed. However, reduced use of coal-tar enamel coating particularly in continental Europe, has been brought about mainly by an increasing awareness of the health hazards involved in the application of the material. The application procedures, properties and uses of buried pipeline coating materials are compared in Table 14.7.

Fusion Bonded Epoxy Powders

After their initial development in the USA, fusion bonded epoxy coatings (FBE) are now factory-applied worldwide. Their specification as the first choice alternative to enamel coatings is still contested, although important

Table 14.7 Comparison of buried pipeline coating materials

<i>Coating type</i>	<i>Applicable standards</i>	<i>Application procedures</i>	<i>Typical system thickness (mm)</i>	<i>Characteristics and uses</i>
Glass fibre reinforced enamels	BS 4147 BS 4164 BS 514 AWWA/ANSI C203	Hot applied in factory and in field by line travel	2.5–6	Asphalts prone to water absorption and root damage. Coal tar resistant to oil products and root damage. Long successful service record, particularly coal tars. Proven under concrete weight coatings.
Cold applied tapes	AWWA C209 ASTM D-1000	By hand or machine, in factory or field	≤2 (single wrap)	Various tapes, allowing suitable choice for individual projects. Particularly useful for coating weld joints, bends, specials in the field. Compatible with all factory coatings.
Polyethylene loose sleeving	AWWA/ANSI C105 BS 6076	By hand in the field	0.2–0.25	Very economical and lightweight. Most commonly utilised over zinc sprayed ductile iron pipes. Will not allow application of effective cathodic protection. May not arrest all corrosion.
Fusion bonded epoxy	AWWA/ANSI C213 BS 3900	Electrostatic spray in factory and for joints in field	0.3–0.65	Higher temperature limitations and superior soil stress resistance compared with enamels. Requires careful handling in the field. Quality of pipe steel important.
Extruded/sintered polyethylene	DIN 30670 DIN 30674	By extrusion or sintering in factory	1.8–3.5	Rugged, heavy coating. Limited track record.
Various thermosetting and thermoplastic resins	BS 3900	Powder/liquid system in factory. Airless spray/trowel in field	≤5	Superior chemical and abrasion resistance compared with enamels. Comparatively expensive. Simultaneous coating internally/externally possible. Various resins available to suit particular requirements.
Heat-shrink crosslinked polyethylene	DIN 30672	Flame or heat gun in field	1.25–2.25	Utilised for coating of field weld joints and repairs on extruded polyethylene coated pipes. Careful application required to achieve consistent bond.

improvements have been made in present powder systems over those first developed.

The thermosetting powders are applied to a white metal blast-cleaned surface by electrostatic spray. Pipe is preheated to approximately 230°C, the quantity of residual heat being directly correlated to the maximum thickness of coating which may be achieved. On application, the powder melts, flows and cures to produce thicknesses in the range 250–650 μm and is then forced cooled by water quenching. Specifications normally place restrictions on pipe bending with thicknesses greater than 450 μm , but nearer maximum thicknesses are required where concrete weight coating is to be applied by impact methods.

Strict control of the fusion process is imperative. In addition to thickness, hardness, continuity and adhesion checks, correct cure may be assessed by differential scanning calorimetry techniques, which are designed to measure any difference in the glass transition temperature of a laboratory-cured powder and the cured coating taken from the factory-coated pipe.

Although in the UK, FBE powders have been chosen in preference to coal-tar enamel coatings where stability at higher temperatures or resistance to soil stress situations has been required, doubts still exist over the powders long-term water absorption characteristics and resistance to cathodic disbondment under high negative cathodic protection potentials. Many of these doubts are being overcome by the inclusion of a precoating chromate conversion treatment provided to the pipe immediately after normal surface preparation. This process has brought about significant improvement to FBE-coated pipe under test for cathodic disbondment and hot water immersion resistance.

When applying epoxy powders special consideration must be given to the quality of the pipe steel. This factor has not posed problems to the heavier enamel coatings. However, due to the comparative thinness of the FBE coating, it is necessary to inspect the metal surface after blast cleaning and vigorously remove all slivers, scabs, gouges and similar defects by grinding to avoid consequential defects in the finished coating.

FBE-coated pipe requires careful handling from factory to the pipe trench to avoid mechanical damage. Repairs are undertaken with either trowel or brush-applied, liquid two-pack epoxy resin-based paints or by melt sticks of compressed powder.

Weld joints may be coated in the field with FBE powder, utilising a portable blast cleaning/induction heating and powder application system. Alternatively joints may be provided with self-adhesive laminate tapes or heat-shrink crosslinked polyethylene sleeves.

Polyethylene Resins

Polyethylene coating on ferrous pipes may be applied by means of one of the following processes: circular or ring-type head extrusion, side extrusion and wrapping or powder sintering. The commercially available coating systems also differ further in that the extruded polyethylene may be applied in conjunction with various primer/adhesive systems.

Generally, systems developed in the USA favour a combination of polyethylene with either butyl-rubber or hot-applied mastic adhesives, the latter consisting of a blend of rubber, asphalt and high molecular weight resins. In European and Far East coating plants, epoxy type primers and 'hard' ethylene copolymer adhesives have been successfully employed.

The specification of these later coatings is covered by the German DIN 30670 standard for steel tubes and DIN 30674 for ductile iron pipes. These standards note that some 1 mm thickness of polyethylene is required for corrosion protection alone, but to improve the mechanical load-bearing capacity of the coating, total thicknesses of 1.8–3.0 mm, depending on pipe diameter, are to be specified.

Repairs to the coating are made with either hot-melt polyethylene sticks or polyethylene sheet patches with mastic profiling compounds for small damaged areas. Large repair areas are best treated as for field weld joint coating, where either heat-shrink crosslinked polyethylene sleeves or cold-applied self-adhesive laminate tapes are employed.

Cold Applied Tapes

In addition to the petrolatum tapes and those based on a laminate of p.e. or p.v.c. with an elastomeric sealant or pressure-sensitive adhesive layer, recent developments have centred around self-adhesive bituminous laminates. These tapes are commonly constructed with a p.v.c. backing, whose thickness ranges from 0.08 to 0.75 mm and a bituminous adhesive compound layer to provide a total tape thickness of up to 2 mm. In order to maintain conformability without compromising impact values, tapes may also be manufactured with a fabric reinforcement within the bituminous layer.

Being self-adhesive these tapes are produced on the roll with a protective paper interleaf designed to be removed as the tape is applied. Application may be by hand or by specially designed hand operated pipe wrapping machines which will accommodate the interleaf. Application is normally undertaken at either 25 mm or 55% overlap depending on the total coating thickness required. Most importantly, bonding at the overlaps will be achieved, as compared with tapes employing elastomeric sealant layers, where contact with fresh primer is required to activate adhesion.

These bituminous tapes are compatible with all factory-applied coatings and thus are particularly employed for weld joint wrapping in the field.

Tapes are produced in both temperate and tropical grades and heavy duty versions can be supplied for application under hot mastic asphalts at field joints of concrete weight-coated pipelines. Wrapping of complex shapes may be achieved by first profiling with a bituminous filler compound.

Other Systems

Thermosetting epoxy and polyurethane chemically-cured liquid resins can provide, among other characteristics, superior abrasion resistance coatings. Solvent-free formulation applied by 'hot' spray techniques can achieve film thicknesses of up to 5 mm.

A typical application of these coatings is the use on carrier pipes installed by thrust boring techniques at major road, rail and river crossings. Sprayed polyurethane coatings of 900 μm thickness, are also commercially available on ductile iron pipes.

Thermoplastic resins, such as vinyl chlorides, vinyl acetates and polyamides are employed, particularly in the water industry, on buried pipes and fittings. To provide both internal and external coating, application may be by one of these principle techniques: dipping in a plastisol, fluidised beds or electrostatic spray.

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D. A. LEWIS

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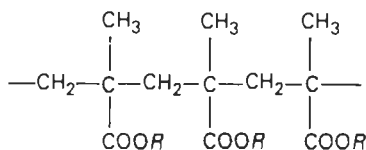
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14.9 Synthetic Resins

The term 'synthetic resin' was coined originally to distinguish these resins from natural resins such as rosin, shellac and the copals. Nowadays nearly all resins used in paint are synthetic, so the first term is often dropped.

There is not enough space here to give a detailed classification, but only to delineate the major families from which resins for industrial coatings may be selected. Resins may be divided into two groups according to their modes of film formation which may or may not involve a chemical reaction. In the first, the components must react together to form a crosslinked structure which may require heat, radiation or catalysis to effect the reaction. The bulk of resins used in industrial finishes are of this type. They are commonly referred to as chemically convertible or, simply, convertible.

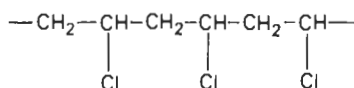
In the second, the components are already of a large size and will form a film by a felting process. Here film formation depends on some physical change such as the loss of solvent by evaporation or heating, or the fusion of a dispersion. Cellulose nitrate is the classic example of a non-convertible resin and still is used extensively because of its unparalleled speed of drying. However, it has a number of disadvantages, being very highly flammable and prone to yellowing. Where better film properties are required, the thermoplastic acrylic resins will give excellent heat and light resistance.



Section of a thermoplastic acrylic resin.
R represents an alkyl group.

Note that the backbone is a chain of carbon atoms which is very resistant to all forms of attack. The side groups determine properties such as solubility, transparency and chemical resistance.

Halogenated resins such as PVC and especially fluorinated resins such as polyvinylidene fluoride show a greater chemical resistance than any other type of resin.



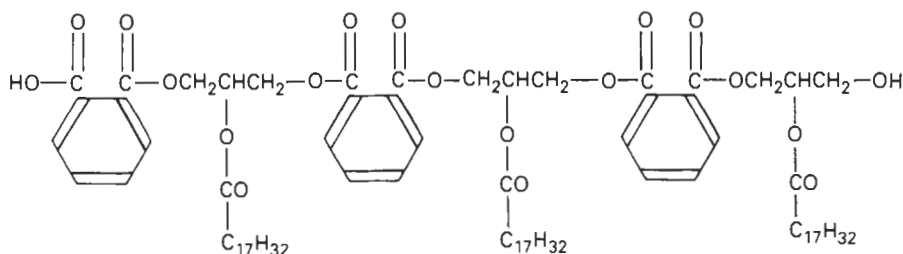
Section of polyvinylchloride resin

Common to all non-convertible, resins is their very low solid content in solution, typically 10–20%, necessitating the application of a number of coats to give an acceptable film thickness unless one is able to use a dispersion rather than a solution of the resin.

The rest of this section will be devoted to the chemically convertible resins. The variety of chemical types exploited in these resins are legion, so only the most widely used will be mentioned here. In some cases a single resin may be employed to produce a coating, but generally blends are used so enabling the film properties to be controlled by ratios of components as well as by choice of the components themselves.

Alkyd Resins and Polyesters

These comprise a large group because almost any acid can be reacted with almost any alcohol to produce an ester which might be suitable as a coating resin. The distinction between an alkyd and a polyester is that the former contains monobasic acids usually derived from vegetable oils such as linseed, soyabean or coconut while the latter do not.

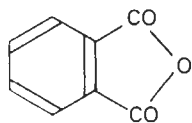


Section of an alkyd resin

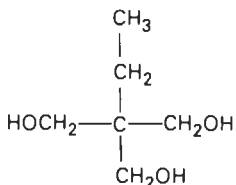
The typical alkyd resin (see above) is comprised of three basic components: an aromatic diacid such as phthalic anhydride which together with a polyol such as glycerol, forms the backbone of the resin molecule and along which are distributed the fatty acids derived from vegetable oils. The solubility, film hardness and colour of alkyd resins depend on the nature of the modifying fatty acid which in most cases contributes some colour to the film.

Today the user industries demand absolute colour stability which has been obtained by developing the so-called oil-free alkyds, also called polyesters

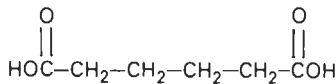
which have excellent colour stability. These are based on mixtures of diacids such as phthalic anhydride and aliphatic diacids such as adipic acid (which promotes extensibility) and a heat-stable polyhydric alcohol such as trimethylolpropane. Structures of these components are shown below.



Phthalic
anhydride

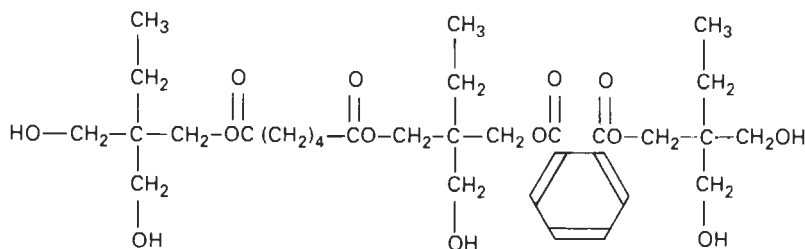


Trimethylolpropane

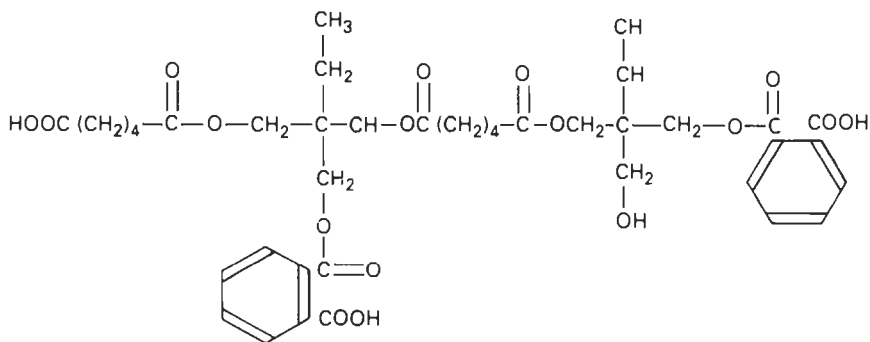


Adipic acid

There are basically two types of polyesters depending on the ratio of acids to polyols used in their preparation, as they may have a predominance of hydroxyl groups or of acid groups. These groups are the sites for crosslinking reactions, for example with formaldehyde resins or reactive isocyanates in the case of the hydroxyl groups or with solid epoxy resins in the case of the acid groups. The latter reaction is exploited in one type of powder coating.



Hydroxyl type polyester resin

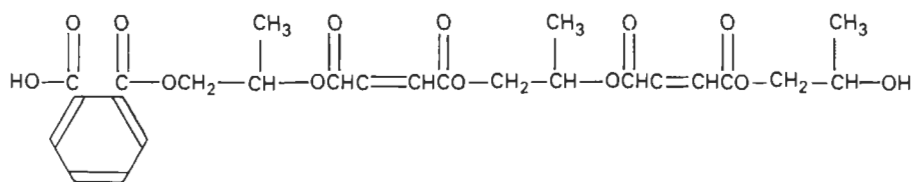


Acid type polyester resin

The resin structures so far depicted represent the basic features of the alkyd and polyester molecules, but other components can be incorporated to enhance one or more film properties as required. One of the most widely used modification is that of vinylation. This is the free radical copolymerisation of unsaturated monomers during the manufacturing stage of the alkyd which must contain a proportion at least of unsaturated fatty acids preferably conjugated as in dehydrated castor oil. The two monomers most used are styrene and methyl methacrylate and the final product may contain up to 35% of combined monomer. This gives alkyds that are faster drying and paler having greater chemical resistance, but having less solvent resistance and outdoor durability than the unmodified alkyds.

Saturated polyesters and saturated alkyds cannot undergo such modification with vinyl monomers but can be modified with other polymers such as silicone resins by alcoholysis. Here outdoor durability is considerably improved.

A further type of ester resin is the unsaturated polyester where the unsaturation is built into the backbone by the use of maleic anhydride:



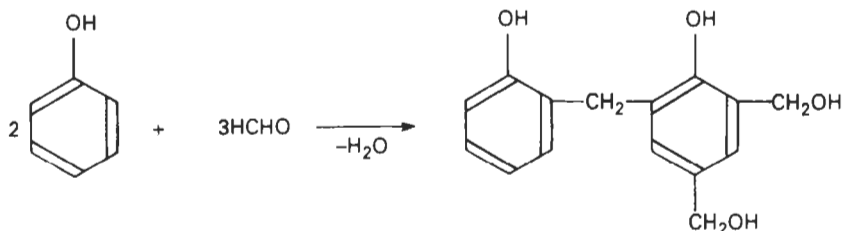
Unsaturated polyester resin

This is a linear polyester containing phthalic anhydride to ensure hydrocarbon solubility and maleic anhydride to enable copolymerisation to take place, esterified with 2-propanediol. The ester is dissolved in styrene which initially acts as the solvent and subsequently as film former when it is copolymerised with the double bond in the ester by free radical induced polymerisation.

Unsaturated polyester finishes of this type do not need to be stored to effect crosslinking, but will cure at room temperature once a suitable peroxide initiator cobalt salt activator are added. The system then has a finite pot life and needs to be applied soon after mixing. Such a system is an example of a two-pack system. That is the finish is supplied in two packages to be mixed shortly before use, with obvious limitations. However, polymerisation can also be induced by ultra violet radiation or electron beam exposure when polymerisation occurs almost instantaneously. These techniques are used widely in packaging, particularly cans, for which many other unsaturated polymers, such as unsaturated acrylic resins have been devised.

Formaldehyde Resins

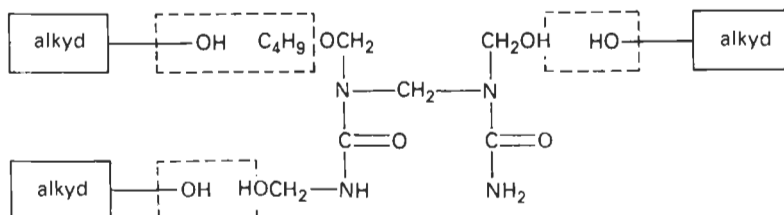
These resins are prepared by an addition reaction of formaldehyde with either phenols, urea or melamine to prepare an intermediate such as the following:



Phenol formaldehyde intermediate

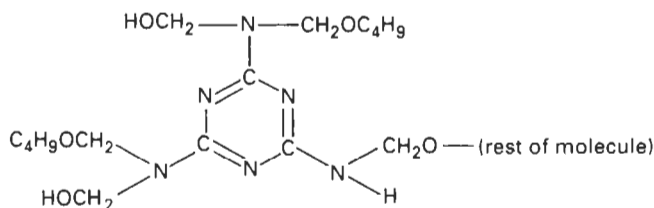
These intermediates are too small to be used alone, but need to be enlarged and modified to obtain compatibility with other resins. In the case of the phenol formaldehyde resins this is achieved by either using *para*-substituted phenols where the substituent contains at least four carbon atoms or by reacting the intermediate with the natural resin, rosin, and then esterifying with glycerol or pentaerythritol. These resins have a limited use in stoved epoxy finishes where colour is not an important factor.

In industrial finishes colour is very important and so a formaldehyde resin based on urea or melamine is usually chosen as both are virtually colourless. Here the intermediates are polymerised in the presence of an alcohol such as 1-butanol which butylates some of the methylol groups. Few of these resins are capable of being used as such in surface coatings and are best considered as crosslinking agents for other resins such as stoving alkyds or thermosetting acrylics. Crosslinking occurs on stoving at about 120°C as follows:



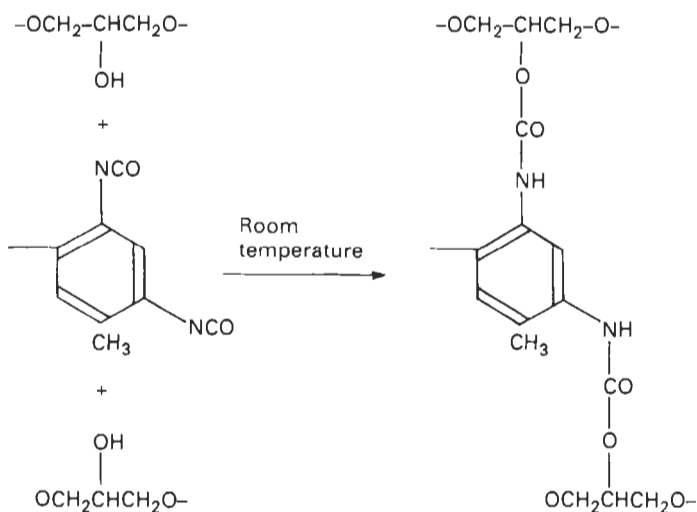
Idealised crosslinking reaction of UF resin with alkyd resin

The melamine resins have many more reactable groups and so less are needed for crosslinking (25% of total compared with 50% of total with UF resins), and have greater heat resistance than the urea resins because of the pseudo-aromatic nature of the six membered ring.



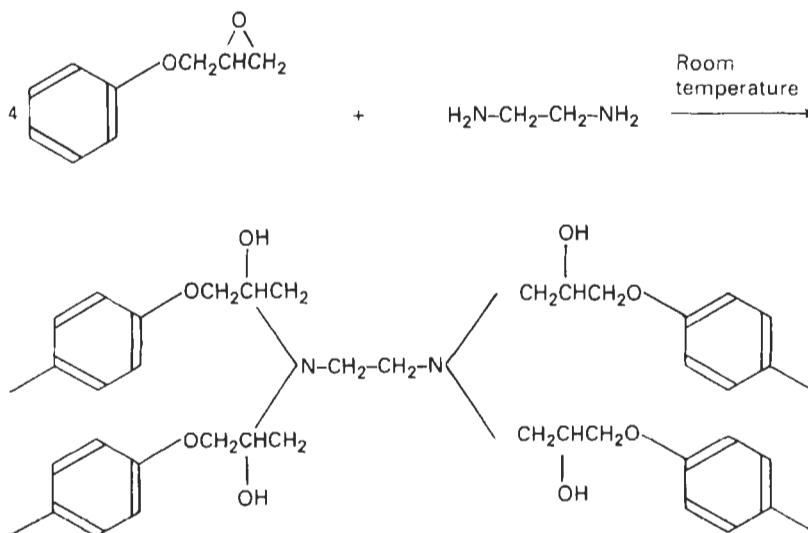
Possible structure of part of an MF resin

The esterification reaction is also used to prepare epoxy esters from epoxy resins having an n value of 4 and vegetable oil fatty acids. They may be used in the same way as alkyds where better chemical resistance and adhesion are required. Unlike the alkyds, the epoxy esters contain virtually no acid groups.



Curing an epoxy resin by reaction with an isocyanate

This reaction is an example of a two-pack epoxy finish where the n value of the epoxy resin is 8 to 12. Although giving a high degree of chemical resistance the reaction is sluggish so the common two-pack finishes are usually based on polyamines with epoxy resins having n values of 0 to 2.



Curing an epoxy resin with a polyfunctional amine

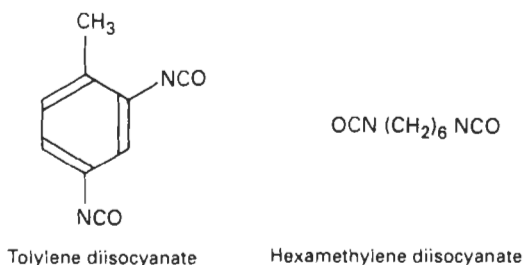
The simplest polyamines are the aliphatic types such as diaminoethane, but these readily carbonate when exposed to the atmosphere as a thin film, so adducts (pre-reacted epoxy polyamines) are preferred. An alternative system is the polyaminoamides which are made by reacting dimerised fatty acids with an excess of polyamine. These themselves act as corrosion inhibitors and are noted for excellent adhesion.

The curing mechanism shown below demonstrates the behaviour of one small polyamine molecule with four epoxy resin molecules. Similar reactions will occur at the other end of the epoxy resin molecules.

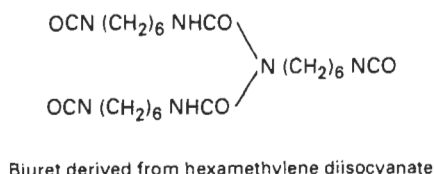
Isocyanate Resins

A variety of types are available, each having different mechanisms of cross-linking but all dependent on the presence of the isocyanate (—NCO) group, either combined or free.

Unlike the epoxy resins where the members differ only in their size, the isocyanate resins differ markedly according to the choice of components, but all have the common feature of a diisocyanate as one of the components. Two of the most widely used diisocyanates are tolylene diisocyanate and hexamethylene diisocyanate which have the following structures:



From these, prepolymers are prepared where the diisocyanates may be completely reacted as in the case of the urethane oils which resemble the oil-modified alkyds but have urethane (—NHCOO—) links in place of the ester (—COO—) links of the alkyds, or where one only of the isocyanate groups is combined, leaving the other to participate in crosslinking reactions. Such a reactive prepolymer is the biuret that may be prepared from hexamethylene diisocyanate, has the following structure:

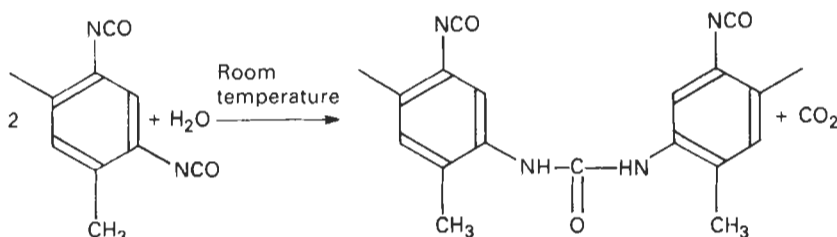


Such reactive isocyanates always contain about 1% by weight of free diisocyanate monomer which is highly toxic, therefore when in use ventilation

must be excellent to maintain the occupational exposure limit below 0.02 ppm.

The isocyanate group is more reactive than the epoxy group in that it will react at room temperature with water and hydroxyl groups as well as with amine groups. However, the latter reaction is too fast to be practicable so the standard two-pack coatings are based on isocyanate and polyhydroxyl prepolymers such as hydroxyl terminated polyesters or polyethers as in the last example given in the section on epoxy resins.

The moisture curing types are one-pack coatings, which, like the two-pack types have excellent chemical resistance and gloss but have a thickness limitation owing to the evolution of carbon dioxide during curing.



Formation of a crosslink by reaction of water and isocyanate group

P. J. BARNES

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14.10 Glossary of Paint Terms*

Adhesion: the degree of attachment between a paint or varnish film and the underlying material with which it is in contact. The latter may be another film of paint (adhesion between one coat and another) or any other material such as wood, metal, plaster, etc. (adhesion between a coat of paint and its substrate). Adhesion should not be confused with 'cohesion' (*q.v.*).

Airless Spraying: the process of atomisation of paint by forcing it through an orifice at high pressure. This effect is often aided by the vaporisation of the solvents especially if the paint has been previously heated. The term is not generally applied to those electrostatic spraying processes which do not use air for atomisation.

Barrier Coat: a coating used to isolate a paint system from the surface to which it is applied in order to prevent chemical or physical interaction between them, e.g. to prevent the paint solvent attacking the underlying paint or to prevent bleeding from underlying paint or material.

Binder: the non-volatile portion of the vehicle of a paint; it binds or cements the pigment particles together, and the paint film as a whole to the material to which it is applied.

Blast Cleaning: the cleaning and roughening of a surface by the use of natural grit or artificial 'grit' or fine metal shot (usually steel), which is projected on to a surface by compressed air or mechanical means.

Blistering: the formation of dome-shaped projections or blisters in paints or varnish films by local loss of adhesion and lifting of the film from the underlying surface. Such blisters may contain liquid, vapour, gas or crystals.

Bubbling: a film defect, temporary or permanent, in which bubbles of air or solvent vapour, or both, are present in the applied film.

Chalking: the formation of a friable, powdery coating on the surface of a paint film caused by disintegration of the binding medium due to disruptive factors during weathering. The chalking of a paint film can be considerably affected by the choice and concentration of the pigment.

Cissing: a defect in which a wet paint or varnish film recedes from small areas of the surface leaving either no coating or an attenuated one.

Cohesion: the forces which bind the particles of a paint or varnish film

* For a full range of definitions see BS 2015:1992.

together into a coherent whole. It is distinct from 'adhesion' (*q.v.*), the forces binding the film to its substrate.

Cracking: generally, the splitting of a dry paint or varnish film, usually as a result of ageing. The following terms are used to denote the nature and extent of this defect:

Hair-cracking. Fine cracks which do not penetrate the top coat; they occur erratically and at random.

Checking. Fine cracks which do not penetrate the top coat and are distributed over the surface giving the semblance of a small pattern.

Cracking. Specifically, a breakdown in which the cracks penetrate at least one coat and which may be expected to result ultimately in complete failure.

Crazing. Resembles checking but the cracks are deeper and broader.

Crocodiling or alligatoring. A drastic type of crazing producing a pattern resembling the hide of a crocodile.

Cratering: the formation of small bowl-shaped depressions in a paint or varnish film.

Extender: an inorganic material in powder form which has a low refractive index and consequently little obliterating power, but is used as a constituent of paints to adjust the properties of the paint, notably its working and film-forming properties and to avoid settlement on storage.

Filiform Corrosion: a form of corrosion under paint coatings on metals characterised by a thread-like form advancing by means of a growing head or point.

Flaking: lifting of the paint from the underlying surface in the form of flakes or scales.

Grinning Through: the showing through of the underlying surface due to the inadequate opacity of a paint film which has been applied to it.

Holidays: skipped or missed areas, left uncoated with paint.

Inhibitive Pigment: a pigment which retards or prevents the corrosion of metals by chemical and/or electrochemical means, as opposed to a purely barrier action. Red lead and zinc chromate are examples of inhibitive pigments as opposed to red iron oxide which has little or no inhibitive action.

Medium: in paints or enamels. The continuous phase in which the pigment is dispersed; thus in the liquid paint in the can it is synonymous with 'vehicle' and in the dry film it is synonymous with 'binder' (*q.v.*).

Opacity (Hiding Power):

(a) *Qualitatively.* The ability of a coat of paint (or a paint system) to obliterate the colour of a surface to which it is applied.

(b) *Quantitatively.* The extent to which a paint obliterates the colour of an underlying surface of a different colour when a film of it is applied by some standard method.

Orange Peel: the pock-marked appearance, in particular of a sprayed film, resembling the skin of an orange due to the failure of the film to flow out to a level surface. (See also *spray mottle*.)

Pigment/Binder Ratio: the ratio of total pigment (white and/or coloured pigment plus extender) to *binder* (*q.v.*) in a paint; preferably expressed as a ratio by volume.

Pinholing: the formation of minute holes in a film during application and drying. Sometimes due to air or gas bubbles in the wet film which burst,

forming small craters that fail to flow out before the film has set.

Pitting: the formation of holes or pits in a metal surface, by corrosion.

Plasticiser: a non-volatile substance, incorporated with film-forming materials in a paint, varnish or lacquer, to improve the flexibility of the dried film.

Pot Life: the period after mixing the two packs of a *two-pack* (q.v.) paint during which the paint remains usable.

Prefabrication Primer: a quick-drying material applied as a thin film to a metal surface after cleaning, e.g. by a blast cleaning process to give protection during the period before and during fabrication. Prefabrication primers should not interfere seriously with conventional welding operations or give off toxic fumes during such operations.

Sagging: a downward movement of a paint film between the times of application and setting, resulting in an uneven coating having a thick lower edge. The resulting sag is usually restricted to a local area of a vertical surface and may have the characteristic appearance of a draped curtain, hence the synonymous term *curtaining*.

Solids (Total Solids): the non-volatile matter in a coating composition, i.e. the ingredients of a coating composition which, after drying, are left behind and constitute the dry film.

Solvent: a liquid, usually volatile, which is used in the manufacture of paint to dissolve or disperse the film-forming constituents, and which evaporates during drying and therefore does not become a part of the dried film. Solvents are used to control the consistency and character of the finish and to regulate application properties.

Spray Mottle: the irregular surface of a sprayed film resembling the skin of an orange. The defect is due to the failure of the film to flow out to a level surface. (See also *orange peel*.)

Tack: slight stickiness of the surface of a film of paint, varnish or lacquer, apparent when the film is pressed with the finger.

Thinning Ratio: the recommended proportion of thinners to be added to a paint or varnish to render it suitable for a particular method of application.

Thixotropic Paint: a paint which while free-flowing and easy to manipulate under a brush, sets to a gel within a short time when it is allowed to remain at rest. Because of these qualities a thixotropic paint is less likely to drip from a brush than other types and can be applied in rather thicker films without running or sagging.

Two-Pack: a paint or lacquer the materials for which are supplied in two parts which must be mixed in the correct proportions before use. The mixture will then remain in a usable condition for a limited time only. The two parts of a two-pack paint are often (though not necessarily) supplied in the correct relative proportion either in entirely separate containers of appropriate sizes or in a single container divided into two compartments; the term '*dual-pack*' is often used to describe the latter type of container.

Zinc-Rich Primer: an anticorrosive primer for iron and steel incorporating zinc dust in a concentration sufficient to give electrical conductivity in the dried films, thus enabling the zinc metal to corrode preferentially to the substrate, i.e. to give cathodic protection.

E. F. REDKNAP
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15 CHEMICAL CONVERSION COATINGS

15.1 Coatings Produced by Anodic Oxidation	15:3
15.2 Phosphate Coatings	15:22
15.3 Chromate Treatments	15:38

15.1 Coatings Produced by Anodic Oxidation

Practice of Anodising

Anodic oxidation or anodising, as applied to metallic surfaces, is the production of a coating, generally of oxide, on the surface by electrolytic treatment in a suitable solution, the metal being the anode. Although a number of metals¹, including aluminium, magnesium, tantalum, titanium, vanadium and zirconium, can form such anodic films, only aluminium and its alloys, and to a lesser extent magnesium, are anodised on a commercial scale for corrosion protection.

The anodic oxidation of magnesium does not normally produce a film that has sufficient corrosion resistance to withstand exposure without further protection by painting, and the solutions used are complex mixtures containing phosphates, fluorides and chromates. In the case of aluminium, a relatively simple treatment produces a hard, compact, strongly adherent film of oxide, which affords considerably increased protection against corrosive attack^{2,3}.

A further advantage of this process lies in the decorative possibilities of the oxide film, which may be almost completely transparent on very high purity aluminium (99·99% Al) and certain alloys based on this purity, and thus protects the surface without obscuring its polish or texture. On metal of lower purity, and other alloys, the oxide layer may become slightly milky, or coloured grey or yellowish, although the deterioration is hardly apparent with purities down to 99·7–99·8% Al. The appearance and character of the film may also be influenced by the type of anodising treatment, and the oxide film may be dyed to produce a wide range of coloured finishes. Anodising characteristics of a number of aluminium alloys are listed by Wernick and Pinner³.

The anodising procedures in general use are shown in Table 15.1, sulphuric acid being the most commonly used electrolyte. Treatment time is 15 min to 1 h.

The articles to be anodised should be free from crevices where the acid electrolyte can be trapped*. They may be given a variety of mechanical and chemical pretreatments, including polishing, satin-finishing, etching, etc. but before anodising, the surface must be clean and free from grease and polishing compound.

*The chromic acid process is preferred where the electrolyte is likely to be entrapped in crevices as it is an inhibitor for aluminium whereas sulphuric acid is corrosive.

Table 15.1 Traditional anodising processes

<i>Electrolyte</i>	<i>Temp (°C)</i>	<i>E.M.F. (V)</i>	<i>Current density (A m⁻²)</i>	<i>Film thick- ness (µm)</i>	<i>Appearance</i>
5–10% (v/v) sulphuric acid	17–22	12–24	110–160	3–25	Transparent, colourless to milky
3–10% chromic acid	30–45	30–45	32	2–8	Opaque, light to dark grey
2–5% oxalic acid	20–35	30–60	110–215	10–60	Transparent, light yellow to brown

After the anodic treatment, the work is removed from the tank and carefully swilled with cold water to remove all traces of acid. At this stage, the anodic film is absorptive, and care should be taken to avoid contamination with oil or grease, particularly if the work is to be dyed. Dyeing may be carried out by immersion for about 20 min in an aqueous solution of the dyestuff at a temperature of 50–60°C. Inorganic pigments may also be incorporated in the oxide layer by a process involving double decomposition. Finally, both dyed and undyed work are sealed by treatment in boiling water (distilled or deionised) or steam, which enhances the corrosion resistance and prevents further staining or leaching of dye. Solutions of metal salts, usually nickel or cobalt acetates, are often used to seal work after dyeing, and sealing in 5–10% dichromate solution, which gives the coating a yellow colour, is sometimes employed where the highest degree of corrosion resistance is desired⁴.

In the architectural field, increasing use is being made of integral colour anodising which is capable of producing self-coloured films in a number of fade-resistant tints ranging from grey, through bronze and brown, to a warm black. The electrolytes are developments of the oxalic acid solution and consist of various dibasic organic acids, such as oxalic, malonic or maleic, or sulphonated organic acids such as sulphasalicylic acid, together with a small proportion of sulphuric acid. For constant and reproducible results, a close analytical control of the electrolyte must be maintained, particularly with respect to aluminium which dissolves as treatment proceeds, and ion-exchange resins are frequently used to regenerate the relatively expensive electrolyte and keep the aluminium in solution between controlled limits. Some typical colour anodising treatments are summarised in Table 15.2*.

Alloys are generally of the Al-Mg-Si type with additions of copper and chromium or manganese. Colour varies with the particular alloy and the film thickness. For optimum control of colour, the alloy must be carefully produced with strict attention to composition, homogenisation and heat-treatment, where appropriate, and the anodising conditions must be maintained within narrow limits. It is usual to arrange matters, preferably with automatic control, such that current density is held constant with rising

*Coloured metal compounds may also be introduced into the film by a.c. treatment in a suitable electrolyte [Fuji process, UK Pat. 1 022 927 (26.2.63)].

Table 15.2 Integral colour anodising processes

<i>Process</i>	<i>Electrolyte</i>	<i>Temp.</i> (°C)	<i>Current density</i> (Am ⁻²)	<i>Voltage</i> (V)	<i>Time</i> (min)
Kalcolor ⁵	Sulphosalicylic acid, 100 g/l	22-25	215-320	25-70	20-45
Duranodic ⁶	Sulphuric acid, 50 g/l 4- or 5-sulphophthalic acid, 75-100 g/l	15-30	130-370	≥70	30
Alcanadox ⁷	Sulphuric acid 8-10 g/l Oxalic acid, 80 g/l to saturation	15-25	130-160	34-67	50-90

voltage up to a selected maximum, after which voltage is held steady; the whole cycle being for a fixed time. Refrigeration of the electrolyte may be necessary to maintain the temperature at the working level, owing to the relatively high wattage dissipation.

Hard anodic films, 50-100 μm thick, for resistance to abrasion and wear under conditions of slow-speed sliding, can be produced in sulphuric acid electrolytes at high current density and low temperature⁸. Current densities range from 250 to 1 000 Am⁻², with or without superposed alternating current in 20-100 g/l sulphuric acid at -4 - +10°C. Under these conditions, special attention must be paid to the contact points to the article under treatment, in order to avoid local overheating.

The films are generally dark in colour and often show a fine network of cracks due to differential expansion of oxide and metal on warming to ambient temperature. They are generally left unsealed, since sealing markedly reduces abrasion resistance, but may be impregnated with silicone oils⁹ to improve the frictional properties. Applications include movable instrument parts, pump bodies and plungers, and textile bobbins.

Decorative self-coloured films¹⁰ can also be produced in sulphuric acid under conditions intermediate between normal and hard anodising.

Continuously anodised strip and wire, which may be given a dyed finish, are produced by special methods, and are now available commercially with a film thickness up to about 6 μm . Uses include electrical windings for transformers and motors, where the light weight of aluminium and the insulating and heat-resistant properties of the film are of value, and production of small or light-section articles by stamping or roll-forming.

Mechanism of Formation of Porous Oxide Coatings

The irreversible behaviour of an aluminium electrode, which readily passes a current when cathodically polarised, but almost ceases to conduct when made the anode in certain aqueous solutions, has been known for over a century.

It has been established that in the case of electrolytes, such as boric acid or ammonium phosphate solutions, in which aluminium oxide is insoluble,

this anodic passivity is due to the formation of a thin compact layer of aluminium oxide whose thickness is proportional to the applied voltage. In neutral phosphate solutions, for example, film growth practically ceases when the thickness corresponds to about 1.4 nm/V^* , and a similar value has been found for many other electrolytes of this type. These thin films have a high electrical resistance, and can withstand several hundred volts under favourable conditions.

In electrolytes in which the film has a moderate solubility, film growth is possible at lower voltages, e.g. in the range 12–60 V, since the rate of formation of the oxide exceeds its rate of solution and current flow continues owing to the different structure of the oxide layer. Electron microscopy has revealed the characteristic porous structure of these films¹¹. The pore diameter appears to be a function of the nature and concentration of the electrolyte and of its temperature, being greatest in a solution of high solvent activity, while the number of pores per unit area varies inversely with the formation voltage. In any given electrolyte, the lower the temperature and concentration, and the higher the voltage, the more dense will be the coating, as both the pore diameter and the number of pores per unit area are reduced under these conditions. Table 15.3, taken from a paper by Keller, Hunter and Robinson¹², illustrates these points.

Table 15.3 Number of pores in anodic oxide coatings

<i>Electrolyte</i>	<i>Temp.</i> (°C)	<i>E.M.F.</i> (V)	<i>Pores/cm² × 10⁻⁹</i>
15% sulphuric acid	10	15	77
		20	51
		30	28
3% chromic acid	49	20	22
		40	8
		60	4
2% oxalic acid	24	20	36
		40	12
		60	6

Note. Data reproduced courtesy *J. Electrochem. Soc.*, **100**, 411 (1953)

In order to account for the relatively high potential required to maintain the current it was suggested by Setoh and Miyata¹³ that a thin *barrier-layer*, similar to that formed in non-solvent electrolytes, is present below the porous layer. This view has been supported by later work involving capacity and voltage-current measurements, which have allowed the thickness of the barrier-layer to be computed¹⁴. As in the case of electrolytes which produce barrier films, the thickness has been found to be proportional to the anodising voltage, but is lower than the limiting growth rate of 1.4 nm/V , and varies with the anodising conditions (Table 15.4).

The structure of the anodic film, according to present views, is shown diagrammatically in Fig. 15.1.

*The limiting thickness expressed in nm/V is of some practical value, but has little theoretical significance — at constant potential the rate of growth, although extremely small, is still finite.

The more or less regular pattern of pores imposes a cellular structure on the film, with the cells approximating in plan to hexagons, each with a central pore, while the bases which form the barrier-layer, are rounded. The metal surface underlying the film, therefore, consists of a close-packed regular array of nearly hemispherical depressions which increase in size with the anodising voltage. The thickness of the individual cell walls is approximately equal to that of the barrier-layer¹².

Table 15.4 Barrier-layer thickness in various electrolytes

<i>Electrolyte</i>	<i>Temp.</i> (°C)	<i>Unit barrier-layer</i> <i>thickness (nm/V)</i>
15% sulphuric acid	10	1.00
3% chromic acid	38	1.25
2% oxalic acid	24	1.18

Note. Data reproduced courtesy *J. Electrochem. Soc.*, **101**, 481 (1954)¹⁴

In view of its position in the e.m.f. series ($E^\circ_{\text{Al}^{3+}/\text{Al}} = -1.66\text{V (SHE)}$), aluminium would be expected to be rapidly attacked even by dilute solutions of relatively weak acids. In fact, the rate of chemical attack is slow, owing to the presence on the aluminium of a thin compact film of air-formed oxide. When a voltage is applied to an aluminium anode there is a sudden initial surge of current, as this film is ruptured, followed by a rapid fall to a lower, fairly steady value. It appears that this is due to the formation of a barrier-layer. Before the limiting thickness is reached, however, the solvent action of the electrolyte initiates a system of pores at weak points or discontinuities in the oxide barrier-layer.

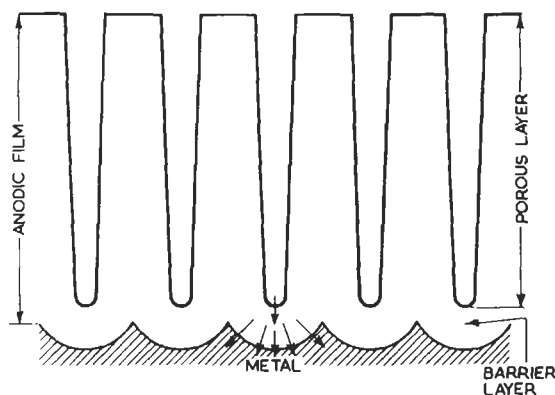


Fig. 15.1 Diagrammatic cross-section of porous anodic oxide film

The formation of pores appears to start along the sub-grain boundaries of the metal, followed by the development of additional pores within the sub-grains. Growth of oxide continues on a series of hemispherical fronts centred on the pore bases, provided that the effective barrier-layer thickness between the metal surface and the electrolyte within the pores, represented by the hemisphere radius, is less than 1.4 nm/V . As anodic oxidation proceeds at

a uniform rate, a close-packed hexagonal cell-pattern is produced, the downward extension of the pore due to solution of oxide keeping pace with the downward movement of the oxide/metal interface, as shown by the arrows in Fig. 15.1. It is fairly clear that the thickness of the individual cell walls cannot exceed the thickness of the barrier-layer if columns of unchanged metal are not to be left behind in the anodic film. The inverse relationship between number of pores and anodising voltage also implies that cells with much thinner walls cannot be formed. Growth of pores in excess of the limiting number appears to be inhibited at an early stage of development, but the actual mechanism is still in doubt.

Radiochemical studies¹⁵ indicate that the pore base is the actual site of formation of aluminium oxide, presumably by transport of aluminium ions across the barrier-layer, although transport of oxygen ions in the opposite direction has been postulated by some authorities¹. The downward extension of the pore takes place by chemical solution, which may be enhanced by the heating effect of the current and the greater solution rate of the freshly formed oxide, but will also be limited by diffusion. It has been shown that the freshly formed oxide, γ' - Al_2O_3 , is amorphous and becomes slowly converted into a more nearly crystalline modification of γ - Al_2O_3 ¹⁶.

Prolonged action of the acid electrolyte on thick films may cause the pores to become conical in section, widening towards the upper surface of the film. This will impose an upper limit on film thickness in solvent electrolytes, as found in practice.

Although it might seem at first sight that dyestuffs are merely held mechanically within the pores, and this view is probably correct in the case of inorganic pigments, there is some support for the opinion that only those dyestuffs which form aluminium/metal complexes produce really light-fast colorations.

The effect of hot water sealing is to convert anhydrous γ - Al_2O_3 into the crystalline monohydrate, $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, which occupies a greater volume and blocks up the pores, thus preventing further absorption of dyes or contaminants. The monohydrate is also less reactive.

Properties of Coatings

Composition The main constituent of the film is aluminium oxide, in a form which varies in constitution between amorphous Al_2O_3 and γ - Al_2O_3 , together with some monohydrate, $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. In the presence of moisture, both the anhydrous forms are gradually transformed into the monohydrate, and the water content of as-formed films is, therefore, somewhat variable.

After sealing in boiling water, the composition of the completely hydrated film obtained when using sulphuric acid approximates to:

Al_2O_3	70
H_2O	17
SO_3	13

It is probable that the SO_3 is combined with the aluminium as a basic sulphate.

Films produced in oxalic acid contain smaller amounts (about 3%) of the electrolyte and only traces of chromium are found in chromic acid films. Sealed films show the electron diffraction pattern of the monohydrate, böhmite.

Density Owing to the variable degree of porosity of the anodic film, it is only possible to determine the apparent density, which varies with the anodising conditions and also with the film thickness.

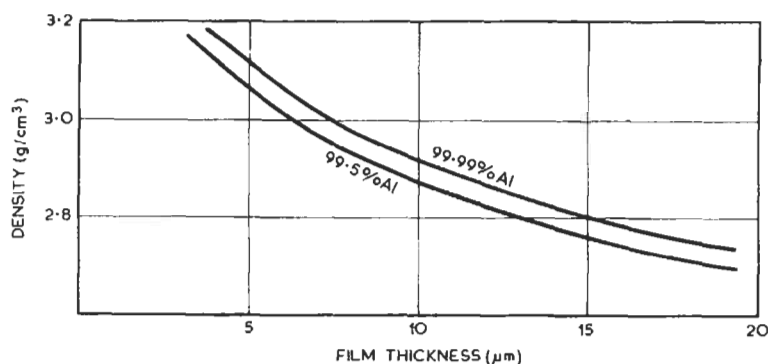


Fig. 15.2 Apparent density of anodic film as a function of film thickness (courtesy *Aluminium*, Berl., 32, 126 (1938))

Fig. 15.2, taken from a paper by Lenz¹⁷, shows the variation in density with thickness for steam-sealed anodic films produced in sulphuric acid on aluminium of 99.99% and 99.5% purity. A mean figure of 2.7 g/cm³ for sealed, and 2.5 g/cm³ for unsealed films is accepted by the British Standard for anodised aluminium¹⁸.

Hardness It is not possible to obtain a reliable figure for the hardness of anodic coatings with either the indentation or scratch methods, because of the influence of the relatively soft metal beneath the anodic film, and the presence of a soft outer layer on thick films. On Moh's Scale, the hardness of normal anodic films lies between 7 and 8, i.e. between quartz and topaz.

Methods are available for the determination of relative abrasion resistance using either a mixed jet of air and abrasive, as recommended in the appropriate British Standard¹⁸ or an abrasive wheel or disc. Owing to variations in the quality of the abrasive, and the performance of individual jets, a standard comparison sample is included in each batch.

The hardness of the film is markedly affected by the conditions of anodising. By means of special methods involving dilute electrolytes at low temperatures and relatively high voltages⁸, with or without superimposed alternating current, it is possible to produce compact abrasion-resistant films with thicknesses of 50–75 μm and hardnesses of 200–500 VPN, for special applications.

Flexibility The normal anodic film begins to crack if subjected to an extension exceeding about 0.5%. Thinner films up to 5 μm in thickness appear to withstand a greater degree of deformation without obvious failure, and are often used for dyed coatings on continuously anodised strip from which

small items may be punched or stamped. Continuously anodised wire can be bent round a radius of 10–15 times its diameter without visible crazing. A greater degree of flexibility is also shown by the more porous coatings produced in 20–25% v.v. sulphuric acid at 35–40°C, while hard films are much less flexible. Unsealed films are only slightly more flexible than films sealed in water or dichromate solution.

Breakdown voltage The breakdown voltage of an anodic film varies with the method of measurement and conditions of anodising, and shows fluctuations over the surface. In the case of unsealed films, breakdown voltage also depends on the relative humidity at the time of measurement. It is normally measured by applying a slowly increasing alternating voltage between a loaded hemispherical probe on the upper surface of the film, and the underlying metal, contact to which may be established by removing a portion of the film¹⁸. The breakdown voltage/thickness relationship for sealed films up to about 20 μm is approximately linear, and the slope of the curve for sulphuric acid films varies from 30 to 40 V/ μm . These results were obtained with a relatively high loading on the probe*; with reduced load (approx. 60 g and below on a hemispherical probe of 1.6 mm radius) values of 60–100 V/ μm can be reached. The higher figures probably represent limiting values which will apply to the conditions between adjacent laps or turns on coils wound from anodised strip or wire.

Resistance The specific resistance of the dry anodic film is

$$4 \times 10^{15} \Omega \text{ cm at } 20^\circ\text{C}^{19}$$

Dielectric constant The dielectric constant of anodic oxide films has been found to be 5.0–5.9 for sulphuric films, and 7–8 for oxalic films. A mean value of 7.45 has been quoted for barrier-layer films¹, but more recent work favours a value of 8.7²⁰.

Thermal expansion The thermal expansion of the film is only about one-fifth that of aluminium¹, and cracking or crazing is observed when anodised aluminium is heated above 80°C. The fine hair-cracks produced do not seem to impair the protective properties of the coating if anodising conditions have been correct.

Heat conduction The heat conductivity of the film is approximately one-tenth that of aluminium².

Heat resistance Apart from hair-cracks, little change is observable in the anodic film on heating up to 300–350°C, although some dyed finishes may change colour at 200–250°C, but at higher temperatures up to the melting point of the metal, films may become opaque or change colour, owing to loss of combined water, without losing their adhesion.

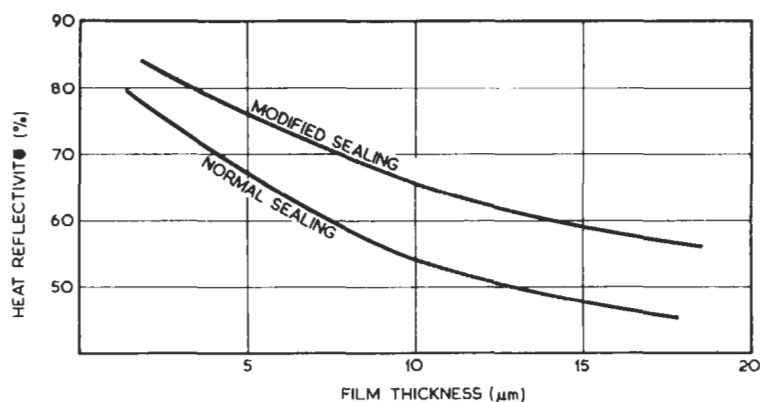
Emissivity Table 15.5 shows the total heat emissivity of various aluminium surfaces, as a percentage of that of a black body. The figures have been recalculated from the data of Hase²¹. The emissivity of anodised aluminium rises rapidly with film thickness up to 3 μm after which the rate of increase diminishes.

*Several hundred grams, BS 1615 suggests 50–75 g.

Table 15.5 Relative heat emissivity of various aluminium surfaces

Surface	Heat emissivity (%)
Highly polished	4.3–6.4
Etched	6.4–8.5
Bright roll finish	5.3–7.4
Matt roll finish	8.5–16
Aluminium paint	17–32
Diecast	16–26
Sandcast	26–36
Anodised, according to film thickness	38–92
Black body	100

Heat reflectivity The heat reflectivity of as-rolled aluminium is about 95%, but this high value may not be maintained for long in a corrosive atmosphere, although it is less affected by surface finish than is optical reflectivity. Anodising reduces the heat reflectivity, owing to absorption by the oxide layer; this effect increases with film thickness. There is a deep absorption trough in the region corresponding to a wavelength of $3\text{ }\mu\text{m}$; this is probably due to the $-\text{OH}$ grouping in the hydrate, the effects of which may be minimised by sealing the heated film in oil instead of water²². This treatment is particularly valuable for heat reflectors in apparatus using sources running at $900\text{--}1\,000^\circ\text{C}$, which show a peak emission in the $2\text{--}3\text{ }\mu\text{m}$ region. Fig. 15.3

**Fig. 15.3** Heat reflectivity of anodised aluminium

shows the heat reflectivity of anodised super-purity aluminium for a source of this type²³, plotted against film thickness. The benefits of the modified sealing treatment are obvious.

Refractive index The refractive index of the clear anodic film produced on aluminium of the highest purity in sulphuric acid is 1.59 in the as-formed condition, rising to 1.62 after sealing²⁴.

Reflectivity The total and specular reflectivities of an anodised aluminium surface are controlled by both the condition of the metal surface, polished

or matt, and the absorption or light-scattering properties of the oxide layer. Total reflectivity may be defined as the percentage of the incident light reflected at all angles, while specular reflectivity is that percentage reflected within a relatively narrow cone with its axis along the angle of reflection. For many years the standard instrument for measuring specular reflectivity has been that designed by Guild²⁵, but more recently a modified gloss head giving rather greater discrimination has been described by Scott²⁶. Other instruments, while placing a number of surfaces of varying specularity in the same relative order, may give different values for the specular reflectivity.

The general brightness of a surface is chiefly dependent upon the total reflectivity T , while specular reflectivity S controls the character of the reflected image. In assessing the subjective brightness of a surface the eye tends to be influenced more by the S/T ratio or image clarity than by the total reflectivity.

For a high degree of specularity, the metal surface must be given a high polish by mechanical means; this may be followed (or replaced) by electrochemical or chemical brightening. When such a brightened surface is protected by anodising, however, insoluble impurities (mainly iron and silicon) present in the aluminium will be incorporated in the anodic film and will increase its tendency to absorb or scatter light. Only metal of the highest purity, 99.99% Al, produces a fully transparent oxide film, while lower purities show decreased total reflectivities and S/T ratios after anodising because of the increased opacity of the anodic film.

Table 15.6 Effect of metal purity and anodic film thickness on reflectivity

Metal purity (%)	Film thickness (μm)					
	2		5		10	
	T	S/T	T	S/T	T	S/T
99.5	80	0.84	79	0.83	77	0.78
99.8	82	0.95	83	0.95	—	—
99.99 (super purity)	84	0.99	84	0.99	84	0.99
Super purity + 0.5 Mg	84	0.98	84	0.98	83	0.97
Super purity + 1.25 Mg	83	0.99	83	0.99	82	0.99
Super purity + 0.7 Mg, 0.3 Si, 0.25 Cu	82	0.99	79	0.98	—	—

Notes. 1. T = total, S = specular reflectivity.

2. Data reproduced courtesy *Met. Rev.*, 2 No. 8 (1957)²³.

Table 15.6, taken from a monograph by Pearson and Phillips²³, demonstrates these effects. The figures were obtained using the Guild meter on electrobrightened and anodised metal.

Effect of anodising on mechanical properties The tensile strength of thin sections may be somewhat reduced by anodising, owing to the brittleness of the coating, but this effect is normally very slight. Thin sheet, less than about 0.6 mm with a relatively thick anodic coating, also has a tendency to break more easily on bending. The incompressibility of the anodic film on the inside of the bend probably enhances this effect, which is also seen on anodised wire.

Anodising should be used with caution on components likely to encounter high stresses, owing to the deterioration in fatigue properties liable to result under these conditions, but under light loading and with the thinner coatings, the reduction is negligible. In some cases²⁷, an actual improvement has been reported.

Friction The coefficient of friction of the sealed anodic film is 0.76, falling to 0.19 after impregnation with silicone oil²⁸. These results were obtained with anodised wire.

Measurement of film thickness The thickness of an anodic film may be determined by a variety of non-destructive methods. Some of these are capable of a high degree of precision, while simpler methods are available for rough sorting. A number of instruments employing the eddy-current principle, with which, after prior calibration, a rapid estimate of film thickness may be made, are now available. With the best instruments, an accuracy of $\pm 1 \mu\text{m}$ can be obtained. For approximate determinations of thickness, the breakdown voltage of the film may be measured. Breakdown voltage shows wide variations with anodising conditions and metal or alloy composition. A separate calibration curve is, therefore, needed for each treatment. Accuracy is comparatively low, rarely being greater than $\pm 2\%$ of the total film thickness.

For control or calibration purposes, film thickness can be determined by mounting a sectioned specimen and measuring the oxide film thickness directly on the screen of a projection microscope at a known magnification. Alternatively, the loss in weight¹⁸ of an anodised sample of known area may be found after the film has been stripped in a boiling solution made up as follows:

Phosphoric acid (s.g. 1.75)	3.5% v/v
Chromic acid in distilled water	2.0% w/v

Immersion for 10 min is usually sufficient to remove the film without the metal being attacked.

Corrosion Resistance

Since the natural passivity of aluminium is due to the thin film of oxide formed by the action of the atmosphere, it is not unexpected that the thicker films formed by anodic oxidation afford considerable protection against corrosive influences, provided the oxide layer is continuous, and free from macropores. The protective action of the film is considerably enhanced by effective sealing, which plugs the mouths of the micropores formed in the normal course of anodising with hydrated oxide, and still further improvement may be afforded by the incorporation of corrosion inhibitors, such as dichromates, in the sealing solution. Chromic acid films, in spite of their thinness, show good corrosion resistance.

The protective action of sulphuric films is mainly controlled by the anodising conditions, compact films formed at temperatures below 20°C in 7% v/v sulphuric acid being more resistant than the films formed at higher temperatures in more concentrated acid. The wider pores of the latter result in less

protection but these films are more readily dyed. Greater protection is also given by thicker films, and a thickness of about 25 μm is generally considered adequate for architectural work in a normal urban environment. In a heavily polluted industrial area, even thicker films may be desirable, while in rural areas some reduction would be permissible. Bright anodised motorcar trim is generally given a film thickness of about 7 μm .

Alumina monohydrate in the mass is very unreactive, being rapidly attacked only by hot sulphuric acid or caustic soda solutions, and the anodic coating shows similar characteristics to some degree. The presence in the film of macropores due to localised impurities or imperfections in the metal and overlying oxide can bring about rapid penetration, owing to the concentration of attack at the few vulnerable points. Metal of good quality specially produced for anodising should therefore be used in order to ensure that such weak points are absent. For vessels and tanks for holding liquids, it may be preferable to use unanodised aluminium, and to accept generalised corrosive attack rather than run the risk of perforation, which may occur with anodised metal.

For ordinary atmospheric exposure, it is usually possible to arrange that thin spots of the film, such as the contact points of the anodising jigs, are located in relatively unimportant positions on the article and are hidden from view.

Since the corrosion resistance of anodic films on aluminium is markedly dependent on the efficacy of sealing (provided the film thickness is adequate for the service conditions), tests for sealing quality are frequently employed as an index of potential resistance to corrosion. While it is admitted that an unequivocal evaluation of corrosion behaviour can only be obtained by protracted field tests in service, accelerated corrosion tests under closely controlled conditions can also provide useful information in a shorter time within the limitations of the particular test environment employed.

Tests for sealing include dye staining tests such as that specified in BS 1615: 1972*, Method *F*, involving preliminary attack with acid, followed by treatment with dye solution. Nitric acid²⁹ or a sulphuric acid/fluoride mixture may be used for the initial attack, and a rapid spot test³⁰ has been developed using the acid/fluoride mixture, followed by a solution of 10 g/l Aluminium Fast Red *B3LW*. Poor sealing is revealed by a deep pink to red spot, while good sealing gives nearly colourless to pale pink colorations. The test can be applied to architectural or other material on site.

Physical tests of film impedance³¹ using an a.c. bridge have also been recommended, although the correlation with corrosion resistance is necessarily empirical. Film impedance increases at an approximately linear rate with sealing time and film thickness.

Exposure of the samples to a controlled moist atmosphere containing sulphur dioxide, as recommended in BS 1615: 1972, Method *H*, is an example of a test bridging the gap between sealing tests and accelerated corrosion tests. After exposure for 24 h at $25 \pm 2^\circ\text{C}$, poorly sealed films show a persistent heavy white bloom, while good sealing produces at the most a slight superficial bloom.

A rapid immersion test in a hot aqueous solution containing sulphur

*A revised version BS 1615: 1987 is now available.

dioxide has also been developed by Kape³² and is specified in BS 1615:1972, Method *E*. Results are similar to those obtained in the preceding test, Method *H*. The method can also be made quantitative by measuring the weight loss.

The accelerated corrosion test in most general use is the CASS test³³ in which the articles are sprayed intermittently with a solution made up as follows:

NaCl	50 g/l
CuCl ₂ , 2H ₂ O	0.26 g/l
Acetic acid to pH	2.8–3.0

The specimens are clamped at an angle of 15° to the vertical in a baffled enclosure maintained at 50°C, and the exposure time is 24–96 h. Corrosive attack of inadequately sealed or thin films is shown by pitting.

An interesting derivative of the CASS test, known as the *Ford Anodised Aluminium Corrosion Test* (FACT)³⁴ has been developed in the U.S.A. This makes use of a controlled electrolytic attack using the CASS solution. The electrolyte is contained in a glass test cell and clamped against the anodised surface with a Neoprene sealing gasket. A d.c. voltage of 200 V in series with a high resistance is maintained between an anode of platinum wire and the aluminium test piece as cathode. The integrated fall in potential across the cell over a fixed period of 3 min as corrosion proceeds and an increasing current flows, is taken as a measure of the corrosion resistance. A British version of this test using simplified circuitry for the integration is available commercially as the *Anodisation Comparator**. Remarkably good correlation has been obtained between the readings of this instrument and the amount of pitting after exposure at a number of outdoor sites³⁵. Comprehensive reviews of sealing techniques including test methods and corrosion behaviour have been published by Thomas³⁶ and Wood³⁷.

The behaviour of samples under the actual conditions of service is the final criterion, but unfortunately such observations take a long time to collect and assess, and the cautious extrapolation of data from accelerated tests must be relied on for forecasting the behaviour of anodised aluminium in any new environment.

Atmospheric Exposure

Table 15.7 shows the effects of thin anodic oxide films on the resistance to industrial and synthetic marine atmospheres (intermittent salt spray) of three grades of pure aluminium. The results are taken from a paper by Champion and Spillett³⁸ and show how relatively thin films produce a marked improvement in both environments.

In an industrial atmosphere, an anodic film only 6.5 μm thick provides a two-fold increase in life over unprotected metal, and the effect under salt-spray conditions is even greater. It is interesting to note that both the industrial atmosphere and salt-spray results show parallel trends.

A similar improvement in expectation of life for thin anodic coatings has

*SIBA Ltd., Camberley, Surrey.

been reported by Phillips³⁹ for 99.5% Al, and for alloys of the following compositions: Al-1.25 Mn; Al-2 Mg-1 Mn; Al-1 Mg-1 Si. The results for a high-copper alloy were less good.

An interesting paper by Lattey and Neunzig⁴⁰ shows that the better the surface finish of the aluminium the thinner the coating required for protection. Neunzig⁴¹ has also studied the effect of the hair-cracks produced by heating or bending on corrosion resistance. Although pitting was initiated by such cracks in thin films (5 μm), serious pitting in thicker films (15 μm) was observed only if anodising had been carried out at 25°C; films produced at 16-17°C were more resistant to corrosive attack. This re-emphasises the importance of maintaining correct anodising conditions for maximum corrosion resistance.

More recently, results of exposure tests for 10 years in a severe industrial environment at Stratford, London, have been reported by the Fulmer Research Institute⁴². A range of pure and alloy specimens, anodised to a maximum film thickness of about 25 μm , was exposed at an angle of 45°.

Table 15.7 Corrosion tests on unprotected and anodised pure aluminium

		Grade 1B (99·5%)		Grade 1A (99·8%)		Super purity (99·99%)		
Corrosive effect		Film thickness (μm)		Film thickness (μm)		Film thickness (μm)		
		0	6·5	0	4	6·5	0	4
Industrial atmosphere (7 years exposure)	Appearance* (life in years)	2·5	5	2·5	5	5	3·5	6
	Mechanical properties† (life in years)	2·75	5·5	3	4·5	6	3	5
	Pitting‡ (depth in mm)	0·18	0·20	0·18	0·25	0·25	0·20	0·13
Marine atmosphere (11 years exposure)	Appearance* (life in years)	<1	4	1	4	5	3	4
	Mechanical properties† (life in years)	5	>11	8	7	>11	>11	>11
	Pitting‡ (depth in mm)	0·30	0·18	0·15	0·33	0·15	0·15	0·08

*No. of years to deterioration of surface appearance to a fixed arbitrary level.

†No. of years to deterioration of mechanical properties to a fixed arbitrary level.

‡Mean depth of pitting obtained statistically.

Corrosion was assessed visually, by determination of weight loss after cleaning, and by reflectivity measurements. All specimens showed signs of pitting, and there was a considerable loss of reflectivity, the under surface being more affected than the upper. A striking feature of the results was the accelerating rate of deterioration in the last five years of exposure. Although none of the samples was completely protected, results were better for the purer specimens and the thicker films.

Maintenance

In architectural work, particular care must be taken to avoid destructive attack of the anodic film by alkaline mortar or cement during erection, and temporary coatings of spirit-soluble waxes, or acetate-butyrate lacquers are frequently applied to window frames and the like to protect against mortar splashes, which in any event should be removed at the earliest possible moment.

The resistance of properly anodised aluminium exposed to the weather can be considerably enhanced by correct and regular cleaning. Deposits of soot and dirt should be removed by washing with warm water containing a non-aggressive detergent; abrasives should not be used. For window frames this washing may conveniently be carried out when the glass is cleaned in the normal way. In such circumstances the life of the coating may be prolonged almost indefinitely, as exemplified by the good condition of the chromic-anodised window frames of Cambridge University Library which were installed in 1933, and of the sulphuric-anodised window frames of the New Bodleian Library, Oxford University, installed in 1938.

Recent Developments

Practice of Anodising

Although there have been few changes in the basic anodising practices, and sulphuric acid is the electrolyte used in most plants, there have been many developments in the pretreatment, colouring and sealing processes associated with anodising.

The trend in architectural applications has been towards more matt finishes, and the sodium hydroxide-based etchants used frequently contain additives such as sodium nitrate or nitrite or sodium fluoride. Chelating agents such as gluconates, heptonates or sorbitol are added to complex the aluminium produced, and other additives such as sulphides may be present in the etchant to complex zinc dissolved from the alloy, and allow it to be used continuously without dumping⁴³.

In terms of anodising itself, the introduction of a standard for architectural applications of anodised aluminium⁴⁴, and the European development of the Qualanod quality labelling scheme for architectural anodising^{45,46}, have been significant factors in the general improvement in the standard of anodising. Both of these standards require the use of thick coatings (20 or 25 μm), which are sealed to a high quality level. The production of such coatings requires good control of operating parameters, particularly the anodising electrolyte temperature, which should be below 21°C⁴⁷.

The field of colour anodising has changed considerably since the late 1960s. At that time the integral colour anodising processes were dominant in architectural applications, and electrolytic colouring was relatively new. Now, mainly because of the high energy costs associated with integral colour processes, electrolytic colouring is by far the most widely used technique.

In order to produce colour by this method, the anodised work is rinsed and transferred to a suitable metal salt solution. The process is electrolytic, and a.c. is passed between the work and a metal or graphite counter-electrode, causing the metal present in the solution to be deposited at the base of the pores of the anodic coating⁴⁸. The height of the metal deposited in the pores controls the depth of colour, and a range of shades is produced by varying the applied voltage and time. Ranges of bronze and black finishes are produced in nickel-, cobalt- or tin-based electrolytes, and pink, maroon or black finishes in electrolytes based on copper. The electrolytes usually contain the appropriate metal sulphate, with many other additives present to adjust or control pH, to improve throwing power, or to make dark colours easier to produce. Nickel and cobalt electrolytes are used at pH values of 4–6, and tin and copper electrolytes at pH values of 1–2; an e.m.f. of the order of 10–20 V and a current density of about 30–50 A/m² are normally required.

The finishes produced have very good light fastness and corrosion resistance, and, unlike integral colour finishes, the shade is largely independent of the aluminium alloy and the anodic film thickness used. The whole range of shades can be produced on films as thin as 5 µm, so the finishes are also being used in trim applications⁴⁹. Many patents and publications in the electrolytic colouring field now exist and they have been reviewed by many authors^{50,51}.

In order to obtain a wider range of coloured finishes, electrolytic colouring processes have been combined with conventional dyeing⁵². The work is anodised normally to the required film thickness, electrolytically coloured in a cobalt- or tin-based electrolyte to a light bronze shade, and then overdyed in an appropriate dyestuff to give muted shades of red, blue, yellow or brown. Again the main application is architectural, and the finishes have good light fastness and durability. An alternative approach to widening the colour range with electrolytic colouring has been the development of finishes based on optical interference effects⁵³, whereby quite different colours can be produced in the same electrolyte. An intermediate treatment in a phosphoric acid anodising electrolyte is normally required, between anodising and electrolytic colouring, to produce these effects.

With the increasing use of colour anodised finishes, sealing quality has become very important, and seal quality tests and standards have all improved. Sealing smut is more visible on coloured than on clear anodised surfaces, and it has become common practice to try to eliminate this chemically, rather than removing it by hand wiping. Approaches to this include dipping in mineral acids after sealing⁵⁴, and adding surface active agents which prevent smut forming^{55,56}.

Sealing is normally carried out in boiling water and the high energy costs involved have led to the development of alternative, lower-energy methods. Approaches have included the use of boehmite accelerators such as triethanolamines to shorten the sealing time⁵⁷, and the use of so-called 'cold' sealing systems. These latter approaches have mainly been developed in Italy⁵⁸, and are based on the use of nickel salts in the presence of fluorides. They are used at a temperature of about 30°C for a time of 15 min, and are claimed to give good corrosion resistance.

Mechanism of Anodising

The development of sophisticated electron-optical techniques now allows the direct observation of the barrier layer and the pore structure of all types of anodic coating. Much of the most relevant work has been carried out at the University of Manchester Institute of Science and Technology, starting with the work of O'Sullivan and Wood⁵⁹, and most recently summarised by Thompson and Wood⁶⁰. The very early stages of pore growth have been extensively studied, and the importance of surface topography and flaw sites in the pre-existing oxide established. Anion incorporation in the film is another important factor affecting film characteristics, and it has been shown that distribution of the anion within the cell wall structure varies from one electrolyte to another.

The mechanism of colouring with integral colour finishes has been shown to depend on the presence of free metallic aluminium in the film, as well as on the inclusion of intermetallic constituents⁶¹. With electrolytic colouring processes, colour is produced by light scattering effects, with the tiny metallic deposits within individual pores acting as light scattering centres⁶². Distribution of metal in the pores varies from one electrolyte to another, and this can affect the corrosion resistance of the final product⁶³.

The mechanism of sealing has been shown to involve an initial dissolution and reprecipitation of hydrated aluminium oxide on the pore walls, pseudo-boehmite gel formation within the pores, and conversion of this to crystalline boehmite at the film surface⁶⁴. The presence of an intermediate layer close to the film surface, in which the identity of the original pores has been lost, has also been recognised⁶⁵.

Properties of Coatings

The hardness and abrasion resistance of anodic coatings have never been easy properties to measure, but the development of a British Standard on hard anodising⁶⁶ has made this essential. Film hardness is best measured by making microhardness indents on a cross-section of a film^{67,68}, but a minimum film thickness of 25 μm is required. For abrasion resistance measurements, a test based on a loaded abrasive wheel⁶⁹, which moves backwards and forwards over the film surface, has improved the sensitivity of such measurements.

Corrosion Resistance

Tests for quality of sealing of anodic coatings have become internationally standardised. They include dye spot tests with prior acid treatment of the surface (ISO 2143:1981 and BS 6161:Part 5:1982), measurement of admittance or impedance (ISO 2931:1983 and BS 6161:Part 6:1984), or measurement of weight loss after acid immersion (ISO 3210:1983 and BS 6161:Part 3:1984, and ISO 2932:1981 and BS 6161:Part 4:1981). Of these the chromic-phosphoric acid immersion test (ISO 3210) has become the generally accepted reference test.

The recent revision of the main anodising standard (BS 1615:1987) has changed it from a 'specification' to a 'method for specifying', but it provides all the information necessary to write an appropriate specification for any anodised product.

The atmospheric corrosion performance of the newer colour anodised finishes is of interest, and several authors have reported tests^{70,71,72}. Long-term weathering of dyed finishes has also been described and this has led to the recommendation of a limited range of special dyes for architectural applications⁷³. Good performance of the combined anodised and electrophoretically deposited clear lacquered finishes, now used very widely in Japan, has also been reported⁷⁴, together with details of the vertical lines used to produce them⁷⁵.

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15.2 Phosphate Coatings

Introduction

The use of phosphate coatings for protecting steel surfaces has been known for over 60 years, and during this period commercial utilisation has steadily increased until today the greater part of the world production of motorcars, bicycles, refrigerators, washing machines, office furniture, etc. is treated in this way. By far the greatest use of phosphate coatings is as a base for paint, although other important applications are in conjunction with oil, grease, wax and spirit stains to provide a corrosion-resistant finish, with soaps to assist the drawing and pressing of steel, and with lubricating oil to decrease the wear and fretting of sliding parts such as piston rings, tappets and gears.

Applications

Phosphate treatments are readily adaptable to production requirements for articles of all sizes, and for large or small numbers. Economical processing can be achieved, for example, by treating thirty car bodies per hour in a conveyerised spray or immersion plant, or by immersion treatment of small clips and brackets. Mild steel sheet is the material most frequently subjected to phosphate treatment, but a great variety of other ferrous surfaces is also processed. Examples include cast-iron plates and piston rings, alloy steel gears, high-carbon steel cutting tools, case-hardened components, steel springs and wire, powdered iron bushes and gears, etc. Phosphate treatments designed for steel can also be used for the simultaneous treatment of zinc die-castings, hot-dipped zinc, zinc-plated and cadmium-plated articles, but if there is a large quantity of these non-ferrous articles it is more economical to phosphate them without the steel.

Phosphate solutions containing fluorides are used for processing steel, zinc and aluminium when assembled together, but chromate solutions are generally preferred when aluminium is treated alone. The increasing use of cathodic electrophoretic painting on steel, however, has led to a reassessment of the basic processes and formulations that might be most effective.

Methods

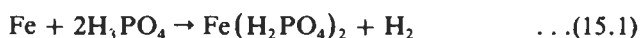
The usual method of applying phosphate coatings is by immersion, using a sequence of tanks which includes degreasing and phosphating stages, with

their respective rinses. The treatment time ranges from 3 to 5 min for thin zinc phosphate coatings up to 30 to 60 min for thick zinc, iron, or manganese phosphate coatings. The accelerated zinc phosphate processes lend themselves to application by power spray, and the processing time may then be reduced to 1 min or less. Power spray application is particularly advantageous for mass production articles such as motorcars and refrigerators, as the conveyor can run straight through the spray tunnel, which incorporates degreasing, rinsing, phosphating, rinsing and drying stages.

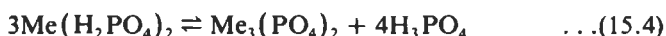
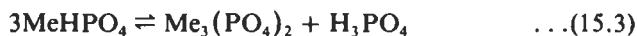
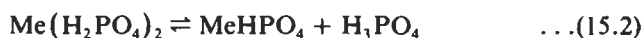
Flow-coating and hand spray-gun application is sometimes employed where a relatively small number of large articles has to be phosphated.

Mechanism of Phosphate Coating Formation

All conventional phosphate coating processes are based on dilute phosphoric acid solutions of iron, manganese and zinc primary phosphates either separately or in combination. The free phosphoric acid in these solutions reacts with the iron surface undergoing treatment in the following manner¹:



thus producing soluble primary ferrous phosphate and liberating hydrogen. Local depletion of phosphoric acid occurs at the metal/solution interface. As the primary phosphates of iron, manganese and zinc dissociate readily in aqueous solution, the following reactions take place:



The neutralisation of free phosphoric acid by reaction 15.1 alters the position of equilibrium of equations 15.2, 15.3 and 15.4 towards the right and thereby leads to the deposition of the sparingly soluble secondary phosphates and insoluble tertiary phosphates on the metal surface.

As reaction 15.1 takes place even when the phosphating solution contains zinc or manganese phosphate with little or no dissolved iron, it will be seen that the simple or 'unaccelerated' phosphate treatment gives coatings which always contain ferrous phosphate derived from the steel parts being processed. After prolonged use, a manganese phosphate bath often contains more iron in solution than manganese and produces coatings with an iron content two or three times that of manganese.

The relation between free phosphoric acid content and total phosphate content in a processing bath, whether based on iron, manganese or zinc, is very important; this relation is generally referred to as the *acid ratio*. An excess of free acid will retard the dissociation of the primary and secondary phosphates and hinder the deposition of the tertiary phosphate coating; sometimes excessive loss of metal takes place and the coating is loose and powdery. When the free acid content is too low, dissociation of phosphates (equations 15.2, 15.3 and 15.4) takes place in the solution as well as at the metal/solution interface and leads to precipitation of insoluble phosphates as sludge. The free acid content is usually determined by titrating with sodium

hydroxide to methyl orange end point, and the total phosphate by titration with sodium hydroxide to phenolphthalein end point. Using this test, non-accelerated processes operated near boiling generally work best with a free-acid titration between 12.5 and 15% of the total acid titration.

A zinc phosphate solution tends to produce coatings more quickly than iron or manganese phosphate solutions, and dissociation of primary zinc phosphate proceeds rapidly through reaction 15.2 to 15.3 or directly to tertiary zinc phosphate via reaction 15.4. Even so, a processing time of 30 min is usual with the solution near boiling.

Another factor in the initiation of phosphate coating reaction is the presence in the processing solution of tertiary phosphate, either as a colloidal suspension or as fine particles². This effect is most apparent in zinc phosphate solutions, which produce good coatings only when turbid. The tertiary zinc phosphate particles can be present to a greater extent in cold processing solutions and act as nuclei for the growth of many small crystals on the metal surface, thereby promoting the formation of smoother coatings.

Similarly, the ferric phosphate sludge formed during the processing of steel in a zinc phosphate solution can play a useful part in coating formation³. The solubility of ferric phosphate is greater at room temperature than at elevated temperatures, and is increased by the presence of nitrate accelerators. To allow for saturation at all temperatures it is desirable always to retain some sludge in the processing bath. Coatings with optimum corrosion resistance are produced when the temperature of the bath is rising and causing super-saturation of ferric phosphate.

With zinc/iron/phosphate/nitrate baths the iron content of the coating comes predominantly from the processing solution and very little from the surface being treated⁴. This greatly diminished attack on the metal surface by accelerated baths has a slight disadvantage in practice in that rust is not removed, whereas the vigorous reaction of the non-accelerated processes does remove light rust deposits.

The solution of iron represented in equation 15.1 takes place at local anodes of the steel being processed, while discharge of hydrogen ions with simultaneous dissociation and deposition of the metal phosphate takes place at the local cathodes¹. Thus factors which favour the cathode process will accelerate coating formation and conversely factors favouring the dissolution of iron will hinder the process.

Cathodic treatment in a phosphating solution exerts an accelerating action as the reaction at all cathodic areas is assisted and the formation of a phosphate layer is speeded accordingly. Conversely, anodic treatment favours only the solution of iron at local anodes and hinders phosphate coating formation. An oxidising agent acts as an accelerator by depolarisation of the cathodes, raising the density of local currents so that rapid anodic passivation of active iron in the pores takes place. This inactivation of local anodes favours the progression of the cathodic process. The accelerating effect of alternating current is explained by the practical observation that the cathodic impulse acting protectively greatly exceeds in its effect the anodic impulse which dissolves iron. In a similar manner the electrolytic pickling of iron with alternating current can dissolve iron at a slower rate than when no current is used.

Reducing agents have the same ultimate effect as cathodic depolarisation in that they convert anodic regions to cathodic and increase the ratio of cathodic to anodic areas.

Nitrogenous organic components such as toluidine, quinoline, aniline, etc. all act as inhibitors to the anodic reaction between metal and acid and thereby favour the cathodic reaction and accelerate the process.

Accelerators

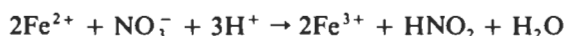
The majority of phosphate processes in use today are 'accelerated' to obtain shorter treatment times and lower processing temperatures. The most common mode of acceleration is by the addition of oxidising agents such as nitrate, nitrite, chlorate and hydrogen peroxide. By this means, a processing time of 1 to 5 min can be obtained at temperatures of 43–71°C. The resultant coatings are much smoother and thinner than those from unaccelerated processes, and, while the corrosion resistance is lower, they cause less reduction of paint gloss and are more suited to mass-production requirements.

Table 15.8 Amount and composition of the gases evolved on phosphating of 1 m² of sheet metal for deep drawing

Phosphate solution	Pointage*	Time (min)	Amount of gas (cm ³ /m ²)	H ₂ (%)	N ₂ (%)	O ₂ (%)	N ₂ O + NO (%)
Manganese phosphate	30	60	7 000	87.5	11.4†	1.1	—
Zinc phosphate	40	30	2 540	92.7	6.4†	0.9	—
Manganese phosphate (accelerated with nitrate)	30	15	3 500	84.6	9.1	1.3	5.0
Zinc phosphate (accelerated with nitrate)	70	5	78	16.7	75.3	8.0	—
Zinc phosphate containing 1.5–2 g/l iron (accelerated with nitrate)	70	5	85	32.1	57.0	1.6	9.3

* A measure of the total of a phosphating solution, as indicated by the number of ml of 0.1 N sodium hydroxide (4.0 g/l) needed to neutralise 10 ml of the phosphating solution to phenolphthalein. † Presumably from nitrides present in the steel.

The presence of nitrate as accelerator has a pronounced effect on the amount and composition of gas evolved from the work being treated¹ (Table 15.8). It will be observed that hydrogen evolution drops to a very low figure with the zinc/nitrate baths. The formation of nitrite arises from decomposition of nitrate by reaction with primary ferrous phosphate to form ferric phosphate:



In an acid solution sodium nitrite acts as a strong oxidising agent by the following reaction:



A slight degree of acceleration can be obtained by introducing traces of metals which are more noble than iron, for example nickel, copper, cobalt, silver and mercury. These metals are deposited electrochemically over the

iron surface undergoing treatment, thereby providing more active cathodic centres and promoting phosphate deposition. This method of acceleration has the disadvantage of leaving minute particles of the noble metal in the coating, and, in the case of copper, this can seriously inhibit the drying of some types of paint coatings. Copper also forms local cells with the iron and so reduces corrosion resistance.

Acceleration by addition of reducing agents, organic compounds, or by application of a cathodic or alternating current, is not nowadays used to any great extent. This situation may change if ways of controlling the $P/(P + H)$ ratio become important (see later).

Nature of Coatings

Effect of Metal Surface

The state of the metal surface has a pronounced effect on the texture and nature of phosphate coating produced by orthodox processes. Heavily worked surfaces tend to be less reactive and lead to patchy coatings. Grit blasting greatly simplifies treatment and gives uniform phosphate coatings. Accidental contamination of sheet steel with lead has been shown to have an adverse effect on the corrosion resistance and durability of phosphate coatings and paint⁵.

Cleaning operations which make use of strong acids or strong alkalis tend to lead to the formation of excessively large phosphate crystals which do not completely cover the metal surface and therefore show inferior corrosion resistance; this is particularly serious if rinsing is inadequate between the preparatory treatment and the phosphating. Adherent dust particles can also lead to the formation of relatively large phosphate crystals, and surfaces which have been wiped beforehand show much smoother and more uniform phosphate coatings.

On the other hand, the provision of vast numbers of minute nuclei assists the phosphate coating reaction to start at a multitude of centres, resulting in a finely crystalline coating. This effect can be obtained chemically by a pre-dip in a solution of sodium phosphate containing minutely dispersed traces of titanium or zirconium salts⁶ or in weak solution of oxalic acid. This type of pre-dip entirely eliminates any coarsening effect due to previous treatment in strong alkalis or acids.

Effect of Phosphate Solution

Improved nucleation within the phosphate solution itself can produce smoother coatings without the necessity of recourse to preliminary chemical treatment. This may be accomplished by introducing into the phosphating bath the sparingly soluble phosphates of the alkaline earth metals or condensed phosphates such as sodium hexametaphosphate or sodium tripolyphosphate. Such modified phosphating baths produce smoother coatings than orthodox baths and are very much less sensitive to cleaning procedures.

Very thin coatings of 'iron phosphate' can be produced by treatment with solutions of alkali metal phosphate. These serve a useful purpose for the

treatment of office furniture, toys, etc. where a high degree of protection is not required, and also as a base for phenolic varnishes, or resin varnishes requiring stoving at over 204°C. The coating is of heterogeneous nature and contains less than 35% iron phosphate ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$) with the remainder probably $\gamma\text{Fe}_2\text{O}_3$.

Thin phosphate coatings can be formed by application of phosphoric acid solution alone, i.e. not containing metallic phosphates, to a steel surface, sufficient time being allowed after application to enable complete reaction to take place. In this way a thin film of iron phosphate can be formed. In practice it is difficult to obtain complete conversion and the remaining traces of phosphoric acid can cause blistering of paint coatings. This effect may be insignificant on rough, absorbent steel surfaces, e.g. ship's plating, where heavy coats of absorbent paint are applied, and under these circumstances the treatment can enhance the corrosion resistance of the finishing system.

Chemical Nature of Coatings

The simplest phosphate coating, that formed from solution containing only ferrous phosphate and phosphoric acid, consists of dark grey to black crystals of tertiary ferrous phosphate, $\text{Fe}_3(\text{PO}_4)_2$, and secondary ferrous phosphate, FeHPO_4 , with a small proportion of tertiary ferric phosphate, FePO_4 . Coatings formed from manganese phosphate solutions consist of tertiary manganese phosphate, and those from zinc phosphating solutions consist of tertiary zinc phosphate. With both the manganese and zinc type of coating, insoluble secondary and tertiary iron phosphates, derived from iron present in the bath, may be present in solid solution. Iron from the surface being treated can also be present in the coating, particularly at the metal/phosphate interface. The PO_4^{3-} content of coatings may vary from 33 to 50%, whereas the theoretical PO_4^{3-} content is lowest, at 41%, in $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ and highest, at 63%, in FePO_4 .

Crystal Structure

It has been suggested that the zinc phosphate coating has the composition $\text{Zn}_3(\text{PO}_4)_2 \cdot \text{Zn}(\text{OH})_2$, but X-ray diffraction studies have given very good correlation between $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ and the zinc phosphate coatings on steel⁸.

$\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ appears in three crystal forms, α -hopeite (rhombic plates), β -hopeite (rhombic crystals), and p -hopeite (triclinic crystals). Their transition points are at 105, 140 and 163°C respectively. It has been observed⁹ that zinc phosphate coatings heated in the absence of air lose their corrosion resistance at between 150 and 163°C.

Manganese phosphate coatings heated in the absence of air lose their corrosion resistance at between 200 and 218°C. At these temperatures, between 75 and 80% of the water of hydration is lost and it is assumed that this results in a volume decrease of the coating which causes voids and thereby lowers the corrosion resistance. Fig. 15.4 shows the loss of water of hydration from zinc, iron and iron-manganese phosphate coatings.

Table 15.9 Analytical tests on industrial phosphate coatings

Process*	P	S	T	Q	V	R
Main cation in phosphate bath	Fe	Mn	Zn	Zn	Zn	Zn
Method of application	Immersion	Immersion	Spraying	Immersion	Immersion	Immersion
Duration of treatment (min)	15	30	1.5	4	5	12
Change in weight on phosphating (g/m^2)	-26.1	-26.4	2.61	3.37	1.63	5.87
Coating weight (g/m^2)	14.2	21.2	4.46	5.43	3.48	12.28
PO_4^{3-} (g/m^2)	7.0	8.9	1.96	2.07	1.20	4.46
Moisture (mg/m^2)	81.5	76.1	152.2	396.6	173.9	771.7
PO_4^{3-} content of coating (%)	49.0	42.0	44.0	38.0	34.0	36.0
Moisture content of coating (%)	0.6	0.4	3.4	6.9	5.0	6.4
Hygroscopicity of coating (%)	0.3	0.2	1.2	1.3	1.0	1.5
Absorption value (diacetone alcohol (g/m^2))	11.4	10.9	10.9	13.04	10.87	11.96

* The letters used for designation indicate proprietary process.

Data reproduced courtesy *J.I.S.I.*, 170, 11 (1952).

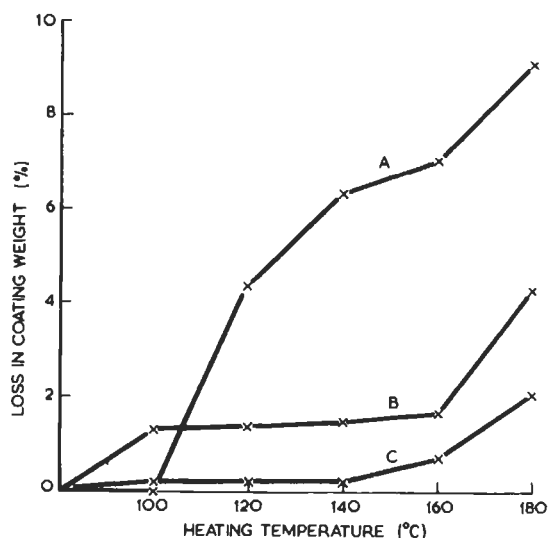


Fig. 15.4 Effect of heating on phosphate coatings for 16 h at various temperatures, showing loss of water of hydration. Curve *A* zinc phosphate, *B* iron phosphate and *C* iron manganese phosphate (courtesy *J.I.S.I.*, 170, 11 (1952))

The heating of phosphate coatings in the absence of air provides conditions similar to those prevailing during the stoving of paint on phosphated articles, but in general the paint stoving temperatures and times are well below those at which damage to zinc phosphate coatings takes place.

The loss of water from conventional zinc and manganese phosphate coatings heated in air is from 10 to 20% higher than the loss on heating in the absence of air. It is thought that this greater loss may be due to oxidation of the iron phosphate present in the coatings.

The most important uses for phosphate coatings entail sealing with oil or paint and it is therefore of interest to study absorption values. Table 15.9 compares the absorption of diacetone alcohol into coatings of widely differing thicknesses and composition; despite these differences, values of 10.8–12.9 g/m² are obtained throughout. It is therefore evident that absorption is predominantly a surface effect and not appreciably influenced by coating thickness.

Rinsing

After phosphating, thorough rinsing with water is necessary in order to remove soluble salts which would otherwise tend to promote blistering under a paint film. Care should also be taken to ensure that the water supply itself is sufficiently free from harmful salts. Experience has shown that a water supply is potentially injurious if it exceeds any one of the three following limits:

1. 70 p.p.m. total chlorides and sulphates (calculated as $\text{Cl}^- + \text{SO}_4^{2-}$).
2. 200 p.p.m. total alkalinity (calculated as CaCO_3).
3. Maximum of 225 p.p.m. of (1) and (2) together.

Improved corrosion resistance and reduced tendency to blistering can be obtained by treating the final rinse with chromic acid, or preferably with phosphoric and chromic acids combined. Normally a total acid content of 0.05% is used. Higher concentrations of chromic acid in the rinse will increase corrosion resistance, partly by passivation of any bare metal or pores in the phosphate coating, but mainly by absorption into the coating^{10,11}. The corrosion resistance rises steadily with increase of chromic acid strength, but above 0.2% chromic acid the phosphate coating tends to dissolve. Absorbed chromic acid is removed only with difficulty by hot or cold water rinsing and is not affected by trichlorethylene vapour treatment. Advantage may be taken of the higher corrosion resistance given by chromic acid, whether or not the metal is to be painted, but care must be taken with white finishing paints, as chromic acid residues may cause local yellowing of the paint in the form of streaks. British Standard requirements for chromic rinsing are shown in Table 15.10.

Table 15.10 Concentration of chromate solution (BS 3189:1973)

Nature of phosphate coating and of sealing coat	Concentration in terms of CrO_3^* (%)	
	Min.	Max
1. Phosphate coatings of all classes to be sealed with paint, varnish or lacquer	0.0125	0.05
2. Zinc phosphate coatings to be sealed with oil or grease	0.0125	0.25
3. Manganese and/or iron phosphate coatings to be sealed with oil or grease	0.0125	0.5

* The substitution of an equal weight of phosphoric acid for up to one half of the chromic acid is permissible.

In recent years there has been a great increase in the use of demineralised water for rinsing, especially before electrophoretic painting. The demineralised water is generally applied by misting jets at the end of all other pre-treatment stages and allowed to flow back into the last rinse tank.

In certain cases rinsing may be dispensed with after non-accelerated phosphate treatment, but blistering of paint due to local concentration of solution in seams and crevices may occur. Rinsing is generally applied, regardless of the type of phosphate process employed¹².

Recent trends are away from rinses containing Cr(VI) and more towards those containing Cr(III) for health and safety reasons.

Corrosion Protection

The corrosion protection provided by phosphate coatings without a sealing treatment is of a low order; their value when sealed is considerably greater. Unsealed corrosion tests are therefore of little value except perhaps for studying porosity or efficiency of coatings destined to be sealed only with oil.

Mention has been made of the necessity for controlling the acid ratio of phosphating baths, particularly those of iron, manganese and zinc operating

Table 15.11 Typical phosphate coating processes

<i>Phosphate coating solution</i>	<i>Accelerator</i>	<i>Immersion time (min)</i>	<i>Type of coating</i>	<i>Coating weight (g/m²)</i>
Iron	None	30	Heavy	10·87–32·61
Iron/manganese	None	30	Heavy	10·87–32·61
Manganese	Nitrate	15	Heavy	8·70–32·61
Zinc	Nitrate	15	Medium	3·26–32·61
Zinc	Nitrate/nitrite or chlorate	3	Light	1·09– 6·52
Sodium/ammonium	None	1–2 (spray)	Very light	0·22– 0·65

near boiling point to produce heavy coatings. At a 'pointage' (see Table 15.8) of 30 in these solutions the free acidity is usually maintained between 12·5 and 15%; above this figure coatings with progressively lower corrosion resistance are obtained.

Heavy phosphate coatings do not necessarily have better corrosion resistance than lighter coatings. Even with a single process, e.g. zinc/iron/phosphate/nitrate, no consistent relationship has been found between corrosion resistance and either coating weight or weight of metal dissolved.

Phosphate processes containing little or no oxidising agent and based on manganese or zinc tend to accumulate iron in solution from the work being processed. With a manganese content of from 0·2% to 0·5% it is best to control the iron at from 0·2 to 0·4%; a higher iron content reduces the corrosion resistance and may lead to the formation of thin powdery coatings, while a lower iron content gives soft coatings. Similarly, a zinc process operates best with 0·15–0·5% zinc and 0·4–0·5% iron. Again, with a higher iron content corrosion resistance falls off and powdery coatings may be formed, and soft coatings result from a lower iron content.

Jaudon¹³ tested phosphate coatings with and without paint and found the salt-spray resistance, as judged by the first appearance of rust, to be as follows:

Bare steel	Few minutes
Phosphated steel	12 h average
Painted steel	150 h
Phosphated and painted steel	300 h

Table 15.12 Typical uses of phosphate coatings on steel

<i>Coating weight (g/m²)</i>	<i>For corrosion resistance</i>	<i>For wear prevention and metal forming</i>
21·74–32·61	—	Critical cold extrusion
10·87–21·74	Military equipment, etc. requiring oil or grease finish	Normal cold extrusion
5·43–10·87	Nuts, bolts, clips, brackets	'Running in' treatment for piston rings, gears and tappets
2·17– 2·72	Cars, refrigerators, washing machines	Wire and tube drawing
1·63– 2·17	Steel drums, bicycles, office machinery	Sheet steel pressing
0·22– 0·65	Toys, office furniture	Light metal pressing
	Strip steel, for painting and forming	

Within broad limits, phosphate processes can be classified according to the main metallic radical of the processing solution and the type of accelerator used; typical processes are given in Table 15.11. The selection of process and of coating weight is mainly dependent on the end-use of the article being processed; the general requirements for corrosion resistance and wear prevention are given in Table 15.12. (See later for comments on $P/(P + H)$ ratio.)

Testing

Heavy phosphate coatings are generally used as protection against corrosion in conjunction with a sealing film of oil or grease. The porosity or free pore area of these coatings should be kept to a minimum. Machu¹⁴ devised a method of examination based on the quantity of electricity necessary to effect passivation of the bare steel and used this to determine the 'free pore area' which, in the phosphate coatings tested, varied from 0.27 to 63%. Attempts to use this method for the evaluation of the more widely used thin zinc phosphate coatings have not been successful, as these coatings show a porosity of less than 1.5% and the technique of measurement was not adequate for this range¹⁵. A method for making rapid measurements of the electrical resistance of phosphate coatings has been described by Scott and Shreir¹⁶.

Akimov and Ulyanov¹⁷ proposed an acidified copper sulphate spot test for assessing the corrosion resistance of phosphated articles by timing the colour change from blue to light green, yellow or red owing to the precipitation of copper. The assumption was that the longer this change took to occur, the higher the corrosion resistance. The test has been thoroughly examined in this country and rejected because of variation in results and poor correlation with corrosion resistance. Sherlock and Shreir^{17(a)} consider that the hydrogen permeation technique could provide a useful means of studying and evaluating the porosity of phosphate coatings.

The most widely used accelerated tests are based on salt spray, and are covered by several Government Specifications. BS 1391:1952¹⁸ (recently withdrawn) gives details of a hand-atomiser salt-spray test which employs synthetic sea-water and also of a sulphur-dioxide corrosion test. A continuous salt-spray test is described in ASTM B 117-61 and BS AU 148: Part 2(1969). Phosphate coatings are occasionally tested by continuous salt spray without a sealing oil film and are expected to withstand one or two hours spray without showing signs of rust; the value of such a test in cases where sealing is normally undertaken is extremely doubtful.

The main value of salt-spray tests is in the evaluation of the effectiveness of phosphate coatings in restricting the spread of rust from scratches or other points of damage in a paint film. This feature is of particular interest to the motorcar industry, as vehicles are often exposed to marine atmospheres and to moisture and salt when the latter is used to disperse ice and frost from road surfaces. Great care is needed in the interpretation of a salt-spray test, as it has been found to favour thin iron phosphate coatings more than is justified by experience with natural weathering. In the motorcar industry the present custom is to use zinc phosphate coatings on the car bodies and all other parts exposed to the outside atmosphere.

Humidity tests are generally of more practical use than salt-spray tests, particularly where painting is employed, as the thoroughness of rinsing may be checked by this means. The use of contaminated water can leave

water-soluble salts in the phosphate coating and lead to blistering of the paint film under humid conditions, as paint films are permeable to water vapour. Immersion in water, or subjection to high humidity in a closed cabinet, will generally show any defects of this kind within a few days. The British Automobile Standard specifies freedom from blistering after 200 h in distilled water at 100°F (38°C).

Table 15.13 Weights of phosphate coatings
(Defence Specification DEF-29)

<i>Class</i>	<i>Type</i>	<i>Minimum coating weight (g/m²)</i>
I	Mn or Fe	7.6
II	Zn, etc.	4.3
III	—	1.6
		0.5*

* A lower range of 0.5 to 1.6 g/m² may be permitted where thin sections are to be fabricated or formed after the application of paint, varnish or lacquer.

The texture or crystal size of phosphate coatings can conveniently be recorded by making an impression on clear cellulose tape moistened with acetone. Uniformity of crystal size is of importance for coatings which are to resist wear and assist metal working. Surface roughness may also be studied by means of a 'Talysurf' meter.

Phosphate coating weight determinations are generally performed by dissolving the coating from weighed panels by immersion in a solution of 20 g/l of antimony trioxide in concentrated hydrochloric acid at a temperature of 13–21°C¹⁹. The solution is used once only. Thin iron or zinc phosphate coatings can be removed for weight determination by immersion in 5% chromic acid solution at 70°C, but this solution should also be used once only, as the presence of more than a trace of phosphate leads to pitting of the steel and false results. Zinc phosphate coatings can be removed by immersion in 10% sodium hydroxide at boiling temperature, aided by rubbing during rinsing.

The Ministry of Defence requirements for phosphating are covered by Defence Specification DEF-29 and are divided into three classes as shown in

Table 15.14 Salt-spray resistance
of phosphate coatings under
various finishes
(Defence Specification DEF-29)

<i>Finish</i>	<i>Period of test (days)</i>
Oil	1
Shellac	1
Lanolin	1
Air-drying paint	3
Stoving lacquer	6
Stoving paint	6

Table 15.13. This specification follows good industrial practice, with additional safeguards in rinsing to remove residues to treatment solutions. Non-accelerated treatments must be followed by a single rinse which may contain chromate; accelerated treatments must be followed by three rinses—cold water, hot water and a final chromate rinse. Table 15.14 shows the salt-spray test requirements for phosphate coatings with various finishes without formation of rust; the paints and lacquer have the additional requirement that no rust shall be visible beyond 0.2 in (5 mm) from the deliberate scratches and no blistering, lifting or flaking beyond 0.05 in (1.27 mm) from the original boundaries of the scratches.

The American Aeronautical Material Specification AMS 2480 A calls for 150 h salt-spray test without rusting extending more than 0.125 in (3.175 mm) on either side of scratch marks, using a black enamel finish for the phosphate coating.

Table 15.15 Weights of phosphate coatings
(BS 3189:1973)

Class of phosphate process	Coating weight (g/m ²)	
	Min.	Max.
A 1. Heavyweight (Mn or Fe)	7.61	—
A 2. Heavyweight (Zn)	7.61	—
B Medium weight (Zn, etc.)	4.34	—
C Lightweight (Zn, etc.)	1.09	4.34
D Extra lightweight (Fe)	0.33	1.09

British Standard 3189:1973¹⁹ contains valuable information on the operation of phosphate processes to obtain optimum results, and on the testing of phosphate coatings. The classification of coatings according to composition and weight is shown in Table 15.15. Recommendations for chromate rinsing are given in Table 15.10. The inspection and testing includes determination of coating weight, freedom from corrosive residues as shown by a humidity test, and resistance to corrosion by salt spray. British Standard 5493:1977²⁰ is also a valuable source of information.

The P/(P + H) Ratio

In recent years considerable interest has been focused on the so-called $P/(P + H)$ ratio in predicting the performance of phosphated steel when coated with cathodic electrophorizer and paint²¹⁻²⁶. In this context, P is defined as the intensity of X-rays diffracted from the (100) plane of a phosphophyllite ($\text{FeZn}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$) at an interplanar spacing d , of 0.884 nm, and H is defined as the intensity of X-rays diffracted from the (020) plane of hopeite ($\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$) at $d = 0.904$ nm. Initial work suggests that high values of this ratio (referred to as the 'The Ratio') are synonymous with good corrosion performance²¹. Later work²²⁻²⁶ indicates that the situation is much more complex than first thought and that many other factors also need to be considered such as method of application,

working temperature, bath chemistry and after-treatment, to name just a few. Reproducible values for The Ratio can be obtained, providing extensive multiple readings are taken in order to take into account topographical variations.

Performance tests²³ show that although the high values of 'The Ratio' appear to be synonymous with good performance, this effect is masked by the use of Cr-containing after-treatments which result in superior corrosion resistance.

Similarly, although dip application shows an overall superiority to spray/dip treatments, good results can be obtained with the latter. Indeed, there may be a reversal of The Ratio trend in this instance²², i.e. performance is slightly inferior at relatively high values of The Ratio. It is also possible to find zinc phosphate coatings exhibiting good performance and high iron content even though X-ray diffraction studies may reveal no phosphophyllite present or crystalline species other than hopeite²¹⁻²⁶. This may be because corrosion resistance is related to a low proportion of hopeite, rather than phosphophyllite, in the coating. Other factors to be considered include the need for homogeneous phosphate layers of controlled thickness, the direct attachment of the primer to a coherent layer (primary phosphate) and the level of interlayer cohesion within the coating. Some papers²⁴ indicate that adhesion failure results from internal fracture of the phosphate coating and that it is concentrated at the junction between a primary microcrystalline or even amorphous layer close to the metal substrate and a secondary layer exhibiting relatively coarse crystallinity. The primary layer is comprised essentially of a zinc phosphate material and the Zn/P ratio in the retained primary layer after fracture is lower than that in the detached material, though close enough to be considered essentially similar.

As already mentioned, acidic chromium-containing rinses for phosphate coatings considerably improve the resistance of paint to water soak and humidity testing. Some authors suggest that the main action is therefore not just the passivating of the regions of steel surface left active after the phosphating process, but could be due to action on the coating itself. If the coating is considered to be a solid alkali comprised of tertiary inorganic phosphates, then it is possible for amorphous phases containing Cr_2O_3 or CrPO_4 to bind the secondary and primary layers together. Similarly improvements in cathodically electropainted systems, in terms of their resistance to water soak tests, are said²⁴ to be obtained by post-rinsing the phosphate surface with dilute acids or even alkalis. This latter effect is only obtained when at least 20–30% of the phosphate surface is actually removed. Thus in such circumstances the secondary phosphate layer is sufficiently depleted to allow the electroprimer direct access to the primary layer. These observations lend support to the notion that, although the potential for good corrosion resistance is greatest with cathodic electroprimer (compared with anodic), the risk of adhesion failure due to internal fracture of the phosphate coating is quite high.

How far the formulation of a phosphating bath influences The Ratio is not entirely clear. Nitrite alone or in combination with chlorate has been the most widely used accelerator system for many years but more recently nitrite-free chlorate/organic systems have been increasingly favoured. Low zinc systems in which the bath is 'starved' of zinc to promote a high iron content in the coating, originally introduced in Japan, have become widespread.

Similarly in Japan there has been a strong move towards full dip treatment and over 50% of car body lines now employ this method. In Europe, while there are some dip-only plants, the majority of recent installations have pre-sprays prior to the dip tank. In the USA spray-only plants still predominate. Zinc phosphate processes normally operate in the range 50–60°C. Low temperature processes operating at 25–35°C are widely used in the UK and Italy but have not been extensively adopted elsewhere.

One area in which there is sometimes confusion is in appreciating exactly what The Ratio signifies. As mentioned above, this is an arbitrary ratio based on intensities of X-rays at very specific diffraction angles. Thus it can be very misleading to assume that the figures quoted are related in some way to the volume or weight fractions of actual hopeite and phosphophyllite crystals present. In extreme circumstances the occurrence of the X-ray peaks may actually move to other diffraction angles. Furthermore, if there is crystal orientation present in a sample then a wide scatter in The Ratio figures will result from alignment problems in the X-ray diffractometer.

Finally, it is worth noting that the quality of the steel substrate can have an effect on the corrosion resistance promoted by any subsequent treatment by phosphating and painting. Indeed, it has been reported²⁷ that interesting results are obtained when cold-rolled steel panels, with different amounts of surface contamination, are zinc phosphated then coated with anionic or cationic electrocoat primers followed by a conventional filler-topcoat system. In salt spray, scab and filiform corrosion tests it is apparently possible to distinguish between different surface contamination levels and primer coatings. Carbonaceous residues on the steel can have a detrimental effect, and this can be confirmed in the case of anionic primer during salt spray tests. In the scab corrosion and filiform corrosion tests, however, anionic primer performance actually increases with surface contamination. It can be concluded that the steel condition and the type of coating affect the corrosion resistance of the entire system by inducing changes in the phosphate layer. With the current low level of surface contamination of commercial steels and the highly resistant modern coating formulations it is suggested²⁷ that the phosphate layer is the weakest link in the entire system.

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15.3 Chromate Treatments

Introduction

The addition of chromates to many corrosive liquids reduces or prevents attack on metals, and chromates are often added to waters in contact with metals as corrosion inhibitors. Under atmospheric exposure an alternative method is used; this consists of depositing on the metal a chromate film which acts as a reservoir of soluble chromate. Although the quantity of chromate which can be held in this way at the metal surface is small, the film nevertheless improves the performance of metals with a high intrinsic corrosion resistance, e.g. cadmium, copper and some aluminium-base materials. With metals which are more liable to corrode, however, such as magnesium alloys and high-strength aluminium alloys, chromate films are used primarily for improving the adhesion of paint, their own inhibiting action making a useful contribution to the total protection.

Chromate treatments can be applied to a wide range of industrial metals. They are of two broad types: (a) those which are complete in themselves and deposit substantial chromate films on the bare metal; and (b) those which are used to seal or supplement protective coatings of other types, e.g. oxide and phosphate coatings. Types of treatment for various metals are summarised in Table 15.16.

Principles of Chromate Treatment

Chromate ions, when used as inhibitors in aqueous solutions, passivate by maintaining a coherent oxide film on the metal surface. Passivation is maintained even in a boiling concentrated chromic acid solution*, in which many of the oxides in bulk form are soluble. The passivity breaks down rapidly, however, once the chromate is removed.

In order that a chromate film may be deposited, the passivity which develops in a solution of chromate anions alone must be broken down in solution in a controlled way. This is achieved by adding other anions, e.g. sulphate, nitrate, chloride, fluoride, as activators which attack the metal, or by electrolysis. When attack occurs, some metal is dissolved, the resulting hydrogen reduces some of the chromate ion, and a slightly soluble golden-brown or black chromium chromate ($\text{Cr}_2\text{O}_3 \cdot \text{CrO}_3 \cdot x\text{H}_2\text{O}$) is formed.

*Vigorous attack can occur with industrial-grade chromic acid, which can contain sulphuric acid as an impurity.

This compound is deposited on the metal surface unless the solution is sufficiently acid to dissolve it as soon as it is formed. The film also usually contains the oxide of the metal being treated, together with alkali metal (when this is present in the treatment solution) perhaps in the form of a complex basic double chromate analogous to zinc yellow.

Table 15.16 Summary of types of chromate treatment

<i>Metal</i>	<i>Type of treatment</i>	<i>Solution, radicals</i>	<i>Type of deposit</i>
Aluminium and its alloys	(a) Alkaline dip	Alkaline chromate	Oxide/hydroxide with perhaps some chromate
	(b) Acid dip, 1	Acid chromate/fluoride/phosphate	Phosphate with perhaps some chromate
	Acid dip, 2	Acid chromate/fluoride/nitrate	Not known, but contains substantial chromate
	(c) Acid pickle	Acid chromate/sulphate and chromate/phosphate	Very thin, may contain chromate
	(d) Sealing of anodic films	Chromate/dichromate in pH range 5 to 7	Blockage of pores with hydroxide/chromate
Cadmium and zinc	Acid dip	Acid chromate/sulphate, sometimes with additions	Thin hydrated chromium chromate
Copper	Acid pickle	Acid chromate/sulphate	Very thin, may contain chromate
Iron and steel	Rinse after phosphate treatment	Dilute acid chromate with or without phosphate	Probably some basic chromate left in the phosphate coating
Magnesium alloys	(a) Strongly acid dip	Acid chromate/nitrate	Thin chromium chromate
	(b) Moderately acid dip	Chromate/sulphate with buffer, pH 4 to 5, also Dow No. 7	Thick chromium chromate
	(c) Slightly acid dip	Chromate/sulphate, pH 6, at boiling or with anodic current	Thick chromium chromate
	(d) Sealing of anodic films	Neutral chromate	Chromate retained by oxide, etc. coating
Silver	(a) Dip	Chromate and complexing salt	Very thin, may contain chromate
	(b) Anodic	Alkaline chromate	Very thin, may contain chromate
Tin	Dip	Alkaline chromate	Very thin, may contain chromate

The stability of the natural oxide film reinforced by the chromate ion determines the conditions of pH, ratio of activating anion to chromate, and temperature at which the oxide is broken down and a chromate film deposited. Thus magnesium alloys can be chromate-treated in nearly neutral solutions, whereas aluminium alloys can be treated only in solutions of appreciable acidity or alkalinity.

The same principle tends to apply to the protective efficiency of the chromate film, i.e. the greater the intrinsic corrosion resistance of the metal, the greater the protection conferred by the soluble chromate in the chromate film.

Aluminium

Chromate Treatment of Aluminium

Several immersion treatments using solutions containing chromates¹ have been developed for aluminium. It is not always clear to what extent the films formed can properly be called chromate films, i.e. films containing a substantial amount of a slightly soluble chromium chromate, but even if the film consists largely of aluminium oxide or hydroxide or other salt with chromate physically absorbed, it will still provide a reservoir of soluble chromate at the metal surface. Treatments fall into two classes: alkaline and acid. The latter are of more recent development.

Alkaline treatments These are all based on the original Bauer-Vogel process in which a boiling solution of alkali carbonate and chromate is used. The best known is the Modified Bauer-Vogel process (DTD 913); others contain silicate (E.W. process), fluoride, chromium carbonate, and/or disodium phosphate (Pylumin processes). The films formed are light to dark grey in colour, depending on the process and the composition of the alloy being treated, and consist substantially of aluminium oxide or hydroxide and probably some soluble chromate, either combined or adsorbed. The protection against mild atmospheres is fair, and is improved by sealing in hot sodium silicate solution. The films produced provide a good basis for paint.

Acid treatments The principal acid processes were developed in the USA under the name Alodine, and are marketed in the UK as Alocrom and under other names. The original solutions were based on acid solutions containing phosphate, chromate and fluoride ions. Immersion for up to 5 min in the cold or warm solution leads to the deposition of a greenish film containing the phosphates of chromium and aluminium, and possibly some hexavalent chromate. The more recent Alocrom 1 200 process uses an acid solution containing chromate, fluoride and nitrate. Room-temperature immersion for 15 s to 3 min deposits golden-brown coatings which contain chromate as a major constituent.

The success of the Alocrom 1 200 process has prompted the introduction of several other commercial processes which deposit similar substantial chromate-bearing films.

Acid pickles Some of the acid pickles used to clean and etch aluminium alloy surfaces and remove oxide and anodic films, such as the chromic/sulphuric acid pickle (method *O* of DEF STAN 03-2) and other chromic-acid bearing pickles (App. *F* of DEF-151) probably leave on the surface traces of absorbed or combined chromate which will give at least some protection against mild atmospheres.

Sealing of Anodic Films

In view of the porous nature of anodic films, especially those produced by the sulphuric acid process (Section 15.1), sealing treatments have been developed in an attempt to improve their protective value. Although not very effective on the relatively dense films produced by the chromic acid process, the sealing treatments enhance the protection afforded by films produced by the sulphuric acid process. For conferring protection against corrosion the most effective treatment is immersion for 5–15 min in a boiling chromate/dichromate solution just on the acid side of pH 8, i.e. at a pH value at which aluminium oxide and hydroxide just begin to be slightly soluble. Defence Specification DEF-151 quotes two solutions, one a 7–10% dichromate/chromate solution at pH 6–7, and the other a 5% dichromate solution containing a small amount of chromate to bring the pH from 4 (dichromate only) to between 5.6 and 6.

The chromate sealing treatment imparts to the anodic film a distinct yellow to brown colour, which is probably due to a basic aluminium chromate or alkali chromate adsorbed on to aluminium hydroxide. The film gives appreciable protection against marine exposure.

Chromate Passivation of Cadmium and Zinc

Cadmium and zinc coatings are widely used to protect steel from rusting, and for preventing accelerated corrosion when two dissimilar metals, e.g. copper and aluminium are in contact. It is important that zinc and cadmium should themselves be preserved from corroding, so that they may give protection by physical exclusion and sacrificial action. The durability of cadmium and zinc coatings depends on their thickness and their intrinsic corrosion resistance under any given exposure. On close-tolerance parts, the thickness is of necessity limited to 25 μm or often appreciably less. Zinc corrodes quite rapidly in humid and marine conditions, and cadmium, though more resistant, is not immune. Both metals are attacked by the organic vapours emitted by some plastics and paints, and by wood². It is therefore often highly desirable to apply a protective coating.

The best protection is given by paint. An etch-primed paint scheme can be applied directly to the metal; for other paints an inorganic treatment must be given to ensure good adhesion. Of the two classes of inorganic treatment, phosphate treatment has little protective value in itself, but chromate passivation gives appreciable protection and in mildly corrosive surroundings may be sufficient in itself.

The most commonly used chromate passivation process is the Cronak process developed by the New Jersey Zinc Co. in 1936, in which the parts are immersed for 5–10 s in a solution containing 182 g/l sodium dichromate and 6 ml/l sulphuric acid. A golden iridescent film is formed on the zinc or cadmium surface. Many variants (all fairly acidic) have been developed subsequently; all are based on dichromate (or chromic acid) with one or more of the following: sulphuric acid, hydrochloric acid (or sodium chloride), nitric acid (or nitrate), phosphoric acid, formic acid and acetic acid. A survey by Biestek³ shows that several of these variants are as good as the Cronak process, although none is superior.

Practical details of the Cronak process are given in Specification DEF-130, and a comprehensive account of the process as applied to zinc plate has been published by Clarke and Andrew⁴. Fig. 15.5 shows the loss of zinc and the

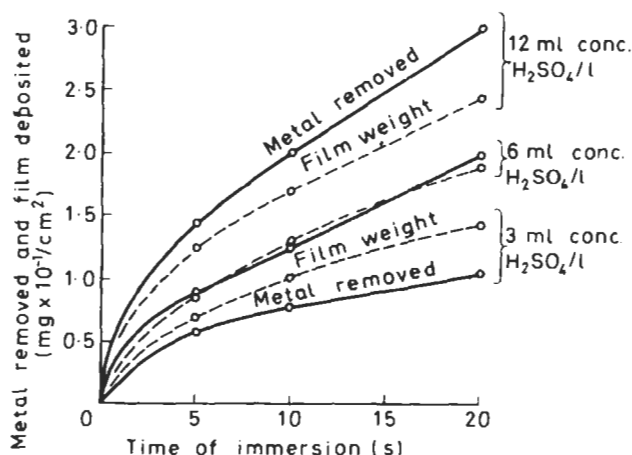


Fig. 15.5 Effect of sulphuric acid concentration on chromate passivation of zinc. Solution: 182 g/l of $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ + H_2SO_4 as indicated; temp. 18°C ; $1.0 \times 10^{-1} \text{ mg Zn/cm}^2 \equiv 0.145 \mu\text{m}$ thickness

weight of film deposited as a function of immersion period and of variation of sulphuric acid content above and below the normal 6 ml/l. The curves show that in the normal bath the weight of film deposited is equal to the weight of zinc dissolved, and that as the acid is consumed, the solution becomes more efficient in converting metal to film. The curves also show that the dissolution of zinc during film formation is small, less than $0.25 \mu\text{m}$, which is an important consideration when small parts such as nuts and bolts are being treated. (On such parts, for reasons of tolerance, relevant specifications are forced to allow minimum thicknesses of down to $4 \mu\text{m}$ of cadmium and zinc plate.)

Claims for other passivation solutions should always be considered in relation to the quantity of metal consumed, unless, of course, the solutions are intended solely for use on zinc-base die-castings, where tolerance on thickness is unimportant.

The chromate film deposited by the Cronak process on zinc consists largely of a hydrated chromium chromate and contains some 10% by weight

of hexavalent chromium, equivalent to 20% of CrO_4^{2-} . At least part of this chromate is soluble in water and available for protecting the underlying zinc or cadmium; on account of this solubility, passivated parts should not be washed in very hot water. Heating at 100°C or higher tends to dehydrate the film and render the chromate in it insoluble, with consequent reduction in protective value; any heat treatment after plating, e.g. for de-embrittlement, should therefore be completed before chromate passivation. If the yellow colour of the chromate film is considered undesirable, treated parts can be subjected to an aqueous extraction 'bleaching' treatment, but much of the protective value will be lost thereby.

The quantitative results quoted above all refer to zinc surface. It is likely that the behaviour of cadmium would be similar; in view of the fact that the equivalent weight of cadmium is double that of zinc, it is even more important that the passivation solution shall not attack and dissolve the metal to any appreciable extent.

Cleaning Etch for Copper and its Alloys

Copper and its alloys can be cleaned and brightened by immersion in solutions of substantial quantities of dichromate with a little acid (see, for instance method *Q* of DEF STD 03-2/1). Such solutions impart some resistance to tarnishing, ascribed to the formation of very thin chromate films.

Clarke and Andrew⁵ have developed a similar solution further activated by addition of chloride ions which deposits more substantial films shown to contain hexavalent chromium. The films give appreciable protection against salt spray and tarnishing by sulphur dioxide.

Iron

Chromate Treatment

In spite of the effectiveness of chromates in stopping the rusting of steel in aqueous solutions, no successful chromate filming process has been developed for this purpose.

Chromate Rinsing of Phosphated Steel

The protective value of a phosphate coating is enhanced by a dip or rinse in an acid chromate solution. Joint Service Specification DEF-29 makes such a rinse mandatory for steel parts treated by an accelerated process, and optional after treatment by a non-accelerated process. Details of rinses are given in Section 15.2 (Table 15.10, p. 15:30).

Magnesium Alloys

(See also Section 4.4.)

Chromate Treatments

Chromates are very effective inhibitors of the corrosion of magnesium alloys by saline and other waters, and many treatments have been developed by means of which substantial films containing slightly soluble chromate are formed in the metal surface. Except on parts which are to be exposed only to a rural atmosphere, chromate treatment must be supplemented by paint, for which it provides a good base.

Magnesium is a relatively reactive metal, and can be chromated in nearly neutral solutions as well as in acid solutions. The range of treatments possible illustrates well the rôle of pH, activating anion, temperature and duration of treatment in promoting the breakdown of passivity in the chromate solution and the consequent formation of a chromate film.

Strongly acid bath This class is represented by a treatment developed in Germany over 60 years ago and widely used since. The solution contains 15% sodium or potassium dichromate and 20–24% v.v. concentrated nitric acid. Parts to be treated are immersed for 30 s to 2 min at room temperature and then allowed to drain for 5 s or more before being washed. Most or all of the film formation occurs during the draining period and the chief function of the immersion period is to clean the surface by etching. The film is thin and of a golden or iridescent grey colour. The process is not suitable for close tolerance parts and is mainly used for protection during storage prior to matching. The process is used in the UK as bath (iv) of DTD 911C, in the USA as the Dow No. 1 treatment and in the USSR as treatment MOKH-1.

Medium acid baths, pH 4–5 At this acidity a dichromate solution plus sulphate ion as activator is sufficient to deposit chromate films in 30 min or so at room temperature or in a few minutes at boiling point. Unfortunately, a solution of alkali dichromate and alkali sulphate is quite unbuffered, and other substances must be added to give the bath a useful life over the working pH range. Acetates have been used successfully, but salts of aluminium, chromium, manganese and zinc have been more commonly employed. The pH of the solution rises slowly during use until basic chromates or sulphates begin to precipitate. The solution can then be rejuvenated by the addition of chromic or sulphuric acid or acid salts.

A successful bath of this class is the Magnesium Elektron Chrome Manganese Bath, bath (v) of DTD 911C, which contains 10% sodium dichromate, 5% magnesium sulphate (as a source of sulphate) and 5% manganese sulphate (as a source of sulphate and as a buffering agent). Treatment is by immersion for up to 2 h at room temperature or up to 10 min at boiling point, the treatment being continued until the appearance of the deposited film has passed the thin golden stage and reached the dark brown to black stage. A second bath of this class is the Dow No. 4 which contains sodium dichromate and potassium chrome alum; this solution is used at boiling point.

The Dow No. 7 treatment, popular in the USA, also falls within this class. The process differs from other chromate treatments in that the activator, magnesium fluoride, is formed on the metal surface by immersion in 20% hydrofluoric acid solution, the parts then being immersed in a 10–15% alkali dichromate solution with or without sufficient alkaline earth fluoride to saturate it. A slow action occurs on the surface and the fluoride film is replaced by a chromate or mixed chromate/fluoride film.

The dichromate solution is quite unbuffered over the working pH range of 4.0–5.5, but the degree of attack on the metal is so slight that in practice appreciable surface areas can be treated before readjustment of the pH by addition of chromic acid becomes necessary. The process is used in the USSR under the code name MFKH-1.

Slightly acid baths, pH 6 At this pH, a boiling temperature must be used to aid the activation of the sulphate present; alternatively, activation can be accomplished by use of an anodic current.

The R.A.E. 'hot half-hour bath', bath (iii) of DTD 911C falls into this class. The solution contains 1.5% each of ammonium and alkali dichromates, 3% ammonium sulphate, and enough ammonia to raise the pH from 4 (dichromate stage) to 6. Parts to be treated are immersed in the boiling solution for 30 min. The solution is well buffered against rise of pH due to magnesium dissolving in the solution, partly by the chemical reaction dichromate \rightarrow chromate, and partly by loss during boiling of ammonia. A closely similar process is used in the USSR under the code name MOKH-6. In the USA the process is applied after a hydrofluoric acid pretreatment, either as above (Dow No. 8 treatment and USSR MFKH-3) or at 50–60°C with the aid of the galvanic current generated when the parts under treatment are connected electrically to the steel tank or to steel cathodes in the solution (Dow No. 9 treatment).

A cold treatment relying on electric current for activation has been developed at R.A.E.; the solution consisted of 15% sodium dichromate and 5% potassium permanganate with added caustic soda to bring the pH to the lower end of the treatment range of 6.0–7.1. Parts were made anode at a current density of 30–80 A/dm² for a treatment time of 20 min.

Chromate Sealing

A large number of electrolytic treatments of magnesium, anodic or a.c., have been developed, in which adherent white or grey films consisting of fluoride, oxide, hydroxide, aluminate or basic carbonate are deposited from alkaline solutions containing caustic alkali, alkali carbonates, phosphates, pyrophosphates, cyanides, aluminates, oxalates, silicates, borates, etc. Some films are thin, and some are relatively thick. All are more or less absorbent and act as good bases for paint, though none contributes appreciable inhibition. All can, however, absorb chromates with consequent improvement of protective efficiency.

The simplest method of chromate sealing involves immersion in a dilute alkali chromate or dichromate solution followed by washing; retained chromate imparts a yellow colour to the film. More substantial amounts of slightly soluble chromate can be deposited in the thicker type of absorbent anodic film by a method developed by Dr. L. Whitby at High Duty Alloys Ltd⁶. In this, anodised parts are immersed first in a boiling 30% solution of sodium chromate and then in a boiling 2% solution of zinc nitrate. Residues of the first solution in the film react with the second solution to give a substantial yellow deposit of a basic zinc chromate, probably similar in composition to zinc yellow.

Silver

Chromate treatments have been developed for protecting silver against sulphide tarnishing by the deposition of very thin films which are assumed to contain chromate. A Dutch-American immersion treatment⁷ uses a chromate solution and a complexing agent, e.g. cyanide, ammonia or E.D.T.A. Working pH values depend on the nature of the agent and lie within the range pH 1-12.

Another treatment consists of making the silver parts cathode in an alkaline chromate solution.

Tin

Alkaline chromate treatments for tin, e.g. the Protecta-Tin processes⁸, have been developed by the Tin Research Institute. The solutions resemble the M.B.V. compositions for treating aluminium, but are more alkaline. Thin invisible films which resist staining by heat and sulphur-bearing compounds and give protection against humid atmospheres at pores are deposited.

Etch Primers

While etch primers, also known as pretreatment primers and wash primers, can be regarded as priming paints which promote their own adhesion by etching the metal surface, they may also be regarded as phosphate/chromate etching treatments which leave an organic residue on the surface to form the basis of the subsequent paint scheme. A detailed account of the etch primers has been given by Coleman⁹.

The standard etch primer (WP-1, DEF-1408) consists of two solutions, one containing polyvinyl butyral resin and zinc tetroxychromate in ethyl alcohol with *n*-butanol, and the second containing phosphoric acid and ethyl alcohol. It is essential that a small critical amount of water be present in the latter. The two solutions are mixed in appropriate ratio for use; the mixture deteriorates and should be discarded when more than 8 h old. Single-pack etch primers of reasonable shelf life are available but contain less phosphoric acid than the above and are not considered to be so effective.

The reactions which take place when the mixed etch primer is applied to a metal are complex. Part of the phosphoric acid reacts with the zinc tetroxychromate pigment to form chromic acid, zinc phosphates and zinc chromates of lower basicity. The phosphoric acid also attacks the metal surface and forms on it a thin chromate-sealed phosphate film. Chromic acid is reduced by the alcohols in the presence of phosphoric acid to form chromium phosphate and aldehydes. It is believed that part of the chromium phosphate then reacts with the resin to form an insoluble complex. Excess zinc tetroxychromate, and perhaps some more soluble less basic zinc chromes, remain to function as normal chromate pigments, i.e. to impart chromate to water penetrating the film during exposure. Although the primer film is hard

enough for over-coating after drying for 1 h, the above reactions continue in the nominally dry film for two to three days, during which time the film remains rather sensitive to water.

Etch priming is widely used on aluminium alloy, and is particularly effective on cadmium and zinc. The adhesion to stainless steel and titanium is good. It has also been used quite widely on bare steel and on magnesium alloy, but on these metals its performance is not, in the opinion of some investigators, always quite reliable. For best protection the etch primer coating is followed with a full paint scheme.

Recent Developments

A comprehensive review by Biestek and Weber¹⁰ covering earlier work on the technology of chromating and the properties of chromate coatings on a range of metals, has been published.

The advent of surface sensitive techniques such as X-ray photoelectron spectroscopy has enabled advances to be made regarding the composition of films formed. Treverton and Davies¹¹ found that the chromate conversion coating on aluminium consisted mainly of Cr(III) with aluminium oxides and fluorides present at the film/substrate interface. Matienzo and Holub¹² have shown that a chromic acid rinse after conversion coating, introduced additional chromium which was incorporated in the coating as Cr(VI). The acid rinse also eliminated fluorides whilst forming a thicker protective layer. Using scanning electron microscopy, Arrowsmith *et al.*¹³ have shown that coatings on aluminium are produced by precipitation of spherical particles which merge and form successive layers. Film growth was maintained by transport of solution through open channels rather than by migration of ions through a continuous layer.

In the case of galvanised steel surfaces, Duncan¹⁴ investigated the composition of the chromate layer after heating, immersion in water and outdoor exposure. Recent developments in zinc coating technology have resulted in the availability of a wide range of compositions. It is known that the formation of suitable conversion coatings on Zn-Ni and Zn-Co electrodeposits is difficult and there is only a limited amount of published information, although several commercial systems are in use. Similarly, zinc coatings produced by hot-dipping, eg. Zn-Al, pose particular problems. Initial work on the conversion coating of different types of zinc substrate prior to powder coating has been reported¹⁵.

Since chromates are highly toxic there has been concern over their discharge into the environment and in the handling of chromate compounds and treated components. This has resulted in increasingly more stringent environmental and factory regulations. The precipitation of Cr(VI) from effluent solutions is difficult and can only be overcome by expensive multi-step treatments. Attempts to comply with legislation have resulted in the development of various new techniques and formulations, but the mechanisms of reaction are still similar to those outlined above. Formulations suggested by Barnes *et al.*¹⁶ use nitrates, hydrogen peroxide or persulphates to initiate metal dissolution, with nitrate being preferred. Successful film-forming compounds include trivalent chromium ions

provided by the leather tanning salt Chrometan, and aluminium ions provided by aluminium sulphate. In the case of chromate solutions a more stable film was produced if a complexant such as sodium hypophosphite was present in solution. LeRoy¹⁷ has developed solutions based on thioglycollic esters where the thioglycolate grouping $\text{HS-CH}_2\text{-C(O)-O-}$ is very reactive with zinc, provided that the zinc surface is clean. Solutions have to be emulsified to stop setting of the polymer and the best coatings are produced when solution pH and temperature are in the range 2–8 and 50–80°C, respectively. The nature of conversion coatings produced on tin and zinc from molybdate and tungstate solutions has been determined and compared with those produced when using chromate solutions (see for example Wilcox and Gabe¹⁸). No-rinse treatments of the organic and inorganic types have been discussed by Matienzo and Holub¹². Dissolution of the metal occurred at low pH followed by deposition of a polymer complex or silica as the pH at the surface increased. Chromium is still introduced from the solution as Cr(III) and Cr(VI), but no acidic rinse followed the formation of the coating.

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16 MISCELLANEOUS COATINGS

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16.1 Vitreous Enamel Coatings

Nature of Vitreous Enamels

A vitreous enamel coating is, as the name implies, a coating of a glassy substance which has been fused onto the basis metal to give a tightly adherent hard finish resistant to many abrasive and corrosive materials. The purpose of modern vitreous enamels is twofold, i.e. to confer corrosion protection to the metal substrate and at the same time to provide permanent colour, gloss and other aesthetic values.

Most of the corrosion resistance, and indeed other properties of the finish, are determined by the composition of the vitreous enameller's raw material *frit*, although other factors can influence them to a minor degree. Frit, for application to sheet and cast iron, is essentially a complex alkali-metal alumino borosilicate and is prepared by smelting together at temperatures between 1 100 and 1 450°C an intimate mixture of refractory materials such as silica, titania, feldspar, china clay, etc. with fluxes exemplified by borax, sodium silicofluoride and the nitrates and carbonates of lithium, sodium and potassium. The smelting continues until all the solid matter has interreacted to form a molten mass, but unlike true glass this liquid does contain a degree of bubbles. At this stage the melt is quenched rapidly by either pouring into water or between water-cooled steel rollers to form 'frit' or 'flake'.

Frit may be milled dry or wet. The long established dry process is used for cast iron baths and for chemical plant. Vitreous enamel application by a dry electrostatic method is being used on an increasing scale. In these cases, the frit is milled alone, or with inorganic colouring or refractory additives. This is achieved in cylinders using balls of porcelain, steatite or more dense alumina, or with pebbles of flint, to produce a fine powder of predetermined size.

In the more common wet process the frit is milled with water, colloidal clay, opacifier, colouring oxide, refractory and various electrolytes in a ball mill to a closely controlled fineness or coarseness.

Typical frit and mill formulae are given in Table 16.1. Frits are tailor-made for each application so that the most desired properties are at their maximum in each case and thus the formulae presented must be regarded as examples of general composition.

Table 16.1 Typical enamel frit compositions (%) and a mill addition

	<i>Chemical plant</i>		<i>Sheet-iron (groundcoats)</i>		<i>Sheet iron (white)</i>	<i>Sheet iron (acid resistant black)</i>	<i>Cast iron (semi-opaque)</i>
Na ₂ O	15.8	17.5	21.8	16.0	7.0	16.0	17.5
K ₂ O	—	—	—	—	5.0	—	3.0
Li ₂ O	—	—	—	—	1.0	1.0	—
CaO	1.2	—	—	—	—	3.0	—
BaO	—	—	—	5.5	—	6.0	—
CaF ₂	3.4	6.0	5.5	4.0	—	2.0	2.0
Na ₂ SiF ₆	—	—	—	—	5.5	2.0	—
Al ₂ O ₃	2.9	5.0	9.0	1.0	2.5	1.0	4.5
B ₂ O ₃	0.9	20.0	18.2	25.0	15.0	7.0	7.5
SiO ₂	60.0	50.0	44.0	47.0	46.0	53.0	43.5
TiO ₂	15.8	—	—	—	18.0	8.0	13.5
CoO	—	0.4	0.3	0.5	—	0.4	—
NiO	—	0.5	0.6	0.5	—	0.6	—
MnO	—	0.6	0.6	0.5	—	—	—
Sb ₂ O ₅	—	—	—	—	—	—	8.5
	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Sheet iron white mill addition

Frit	100	} Grind to fineness of 1 g residue on 200 mesh sieve (50 ml sample)
Water	35-40	
Titania	1	
Clay	2.5	
Bentonite	0.3	
Sodium nitrite	0.05	
Potassium carbonate	0.1	

Metal and Metal Preparation

To obtain a defect-free finish it is essential that the basis metal is of the correct composition and suitably cleaned.

Cast Iron

For cast iron enamelling the so-called grey iron is preferred. Its composition varies somewhat depending upon type and thickness of casting, but falls within the following limits: 3.25-3.60% total C, 2.80-3.20% graphitic C, 2.25-3.00% Si, 0.45-0.65% Mn, 0.60-0.95% P and 0.05-0.10% S.

The standard method of cleaning cast iron for enamelling is by grit or shot blasting which may be preceded by an annealing operation.

Steel

Two general types of sheet steel are in current use, viz. cold-rolled mild steel and decarburised steel. A typical analysis for cold-rolled steel is 0.1% C, 0.5% Mn and 0.04% S. It can be obtained in regular, deep drawing or extra-deep drawing grades. This type of steel is normally used with a ground-coat including cobalt and nickel, as shown in Table 16.1.

Decarburised steel is a mild steel that has undergone a heat treatment in a controlled atmosphere to reduce the carbon content to about 0.005%. This type of steel can be used for white or coloured enamel direct to steel.

Sheet steel is normally prepared for application of enamel by a sequence of operations including thorough degreasing, acid pickling and neutralisation. A nickel dip stage is often included to deposit a thin, porous layer of nickel applied at about 1 g/m^2 , especially when conventional groundcoat is not used (see Section 13.7).

Enamel Bonding

For effective performance the enamel must be firmly bonded to the underlying metal and this bond must persist during usage. The bond is formed by the molten enamel flowing into the 'pits' in the metal, i.e. mechanical adhesion, and by solution of the metal in the glass, i.e. chemical adhesion. The coefficient of thermal expansion of the enamel in relation to the cast iron or sheet steel and enamel setting temperature determines the stress set up in the coating. As enamel, like glass, is strongest under compression, its thermal expansion should be slightly less than the metal.

Enamel Application and Fusion

Vitreous enamel is normally applied to the prepared metal or over a groundcoat by spraying or dipping. Alternative wet techniques are used, of which the most common has been electrostatic wet spraying. Electrophoretic deposition from the slurry has been found to be highly suitable for some components.

On sheet iron a groundcoat, including cobalt and nickel, is generally used, but for mass production (e.g. cookers) use of decarbonised steel and direct application of colours is more common. This involves a more complex steel pretreatment.

After drying the applied slurry, the enamel is fused onto sheet steel at about 800–850°C for about 4–5 min. For cast iron a longer time and lower temperature are normal.

The old dry process enamelling of cast iron (baths etc.) is no longer widely used. The method consisted of sieving finely powdered frit onto the preheated casting and inserting the casting back into a furnace at about 900°C to produce the smooth finish.

In recent years increasing use has been made by many manufacturers, who require a limited range of colours, of the electrostatic application of a dry powder spray. Dry electrostatic finishes are fused at temperatures in the same range as conventional ones.

Properties of Enamel Coatings Affecting Corrosion

Mechanical Properties

This group includes such items as surface hardness, i.e. scratch and abrasion resistance, adhesion and resistance to chipping, crazing and impact. All of

these and other properties depend upon the adhesion between the vitreous enamel layer and the metal being good and remaining so.

There is no single test that will give a quantitative assessment of adhesion, and those which have been proposed all cause destruction of the test piece. It has already been stated that this property is dependent upon mechanical and chemical bonds between the enamel and the metal. One must, however, also consider the stresses set up at the interface and within the glass itself during cooling after fusion or after a delayed length of time.

The coefficient of thermal expansion is primarily determined by the frit composition, although mill additions can have a minor influence. As a general rule, superior acid and thermal shock resistance obtain with low expansion enamel, and the skill of the frit manufacturer is to obtain good resistance and also to maintain a sufficiently high expansion to prevent distortion of the component (pressing or casting). Several workers have produced a set of factors for expansion in relation to the enamel oxides that constitute the frit, which provides a guide to the frit producer. However, as these factors are derived from a study of relatively simple glasses smelted to homogeneity it must be emphasised that they are only a guide. The effect of substituting certain oxides for others in a standard titanium superopaque enamel is given in Table 16.2. The use of a nickel dip improves adhesion by minimising iron oxide formation, but it should be noted that some iron oxide formation is necessary to produce enamel/metal adhesion. In the commonest methods of testing for adherence to sheet iron, the coated metal is distorted by bending, twisting or impact under a falling weight. In the worst cases the enamel is removed leaving the metal bright and shiny, but in all others a dark coloured coating remains with slivers of fractured enamel adhering to a greater or lesser degree. With cast iron enamelling it is not possible to distort the metal and in this case an assessment of adhesion is obtained by dropping a weight on to the enamel surface and examining for fractures. Erroneous results can obtain in that often thicker enamel coatings appear to be better bonded and resistant to impact, whereas in fact the converse is true. Providing the bond is adequate this test really gives an indication of the strength of the enamel itself.

Table 16.2 Effect of frit ingredients on enamel expansion

<i>Constituent varied</i>	<i>Expansion change</i>
Increase alkali metal	Increase
Replace Na_2O by Li_2O	Increase
Replace Na_2O by K_2O	Decrease
Increase fluorine	Decrease
Increase B_2O_3	Decrease
Replace SiO_2 by TiO_2	Increase
Increase TiO_2	Slight increase
Replace SiO_2 by Al_2O_3	Slight increase
Introduce P_2O_5	Slight increase
Introduce BaO	Increase
Increase SiO_2	Decrease

According to Andrews¹ a typical sheet iron groundcoat has a tensile strength of about 10 kg/mm². In small cross section, however, the tensile strength of glass is improved and fine threads, e.g. as in glass fibre, are quite strong. Enamels under compression are 15–20 times stronger than an equal thickness under tension.

The hardness of an enamel surface is an important property for such items as enamelled sink units, domestic appliances, washing machine tubs which have to withstand the abrasive action of buttons, etc. On Moh's scale most enamels have a hardness of up to 6 (orthoclase). There are two types of hardness of importance to users of enamel, viz. surface and subsurface. The former is more important for domestic uses when one considers the scratching action of cutlery, pans, etc. whereas subsurface hardness is the prime factor in prolonging the life of enamelled scoops, buckets, etc. in such applications as elevators or conveyors of coal and other minerals.

Of the several methods of measuring this property those specified by the Porcelain Enamel Institute and the Institute of Vitreous Enamellers are the best known and most reliable. They both consist of abrading a weighed enamel panel with a standard silica or other abrasive suspended in water and kept moving on an oscillating table with stainless steel balls. The loss in weight is measured periodically and a graph of time versus weight loss indicates both the surface and subsurface abrasion resistance. Pedder² has quoted relative weight loss figures for different types of enamel and they are shown in Table 16.3.

Fine bubbles uniformly distributed throughout the coat improve elasticity and thus mill additions and under and over firing influence this property. The greatest effect on elasticity is enamel thickness and most developments are aimed at obtaining a satisfactory finish with minimum thickness.

Appen *et al.* have produced factors for calculating the elastic properties of enamel.

Table 16.3 Comparison of abrasion resistance of different enamels*

<i>Types of enamel</i>	<i>Average loss in weight (g)†</i>
Acid resisting titania based	56×10^{-4}
Acid resisting non-titania	342×10^{-4}
Antimony white cover coat	582×10^{-4}
High refractory enamel	129×10^{-4}
Plate glass	70×10^{-4}

* Table after Pedder².

† Overall figure for tests under standardised conditions for each grade of enamel.

Thermal Properties

These properties are made use of in many applications ranging from domestic cookers to linings which must withstand the heat from jet engines. There is simple heat resistance, i.e. the ability of the enamel to protect the

underlying metal from prolonged heat and also thermal shock resistance, which is the ability to resist sudden changes in temperature without failure occurring in the coating. These thermal properties depend upon the relative coefficient of thermal expansion of enamel and metal, enamel setting point, adhesion, enamel thickness and geometry of the shape to which the finish is applied.

It is obvious that the adhesion must be good in order to prevent rupture at the enamel/metal interface during heating and cooling. Thick coatings are liable to spall when subjected to thermal change due to differential strain set up within the enamel layer itself, caused by the poor heat conductivity of the glass. Thus again thin coatings are desirable.

Compressive forces on enamel applied to a convex surface are less than when a concave surface is coated, and it is therefore apparent that the sharper the radius of the metal the weaker the enamel applied to it will be. This fact is also relevant to mechanical damage.

Thermal shock resistance is important for gas cooker pan supports and hotplates where spillage is liable to occur, but in oven interiors heat resistance is more relevant.

The softening point of conventional cast and sheet iron enamels is about 500°C, but special compositions are obtainable which operate successfully at 600°C. Other more specialised enamels withstand service conditions ranging from being in excess of dull red heat, e.g. as obtained in fire backs, to those capable of enduring short exposure to temperatures of around 1 000°C, e.g. in jet tubes, after burners, etc.

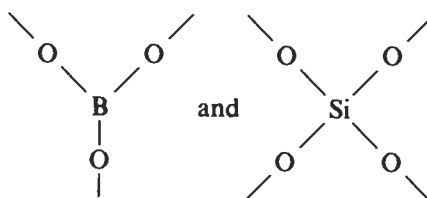
Chemical Resistance

That examples of glass and glazes manufactured many centuries ago still exist is an indication of the good resistance of such ceramics to abrasion, acids, alkalis, atmosphere, etc.

In this section, chemical resistance will be divided into three parts, viz. acid, alkali (including detergents) and water (including atmosphere). Normally an enamel is formulated to withstand one of the corrosive agents more specifically than another, although vitreous enamel as a general finish has good 'all round' resistance, with a few exceptions such as hydrofluoric acid and fused or hot concentrated solutions of caustic soda or potash.

Acid resistance This property is best appreciated when the glass structure is understood. Most enamel frits are complex alkali metal borosilicates and can be visualised as a network of SiO_4 tetrahedra and BO_3 triangular configurations containing alkali metals such as lithium, sodium and potassium or alkaline earth metals, especially calcium and barium, in the network interstices.

Fused silica may be regarded as the ultimate from the acid resistance aspect but because of its high softening point and low thermal expansion it cannot be applied to a metal in the usual manner. Rupturing or distorting this almost regular SiO_4 lattice makes the structure more fluid. Thus to reduce its softening point B_2O_3 is introduced whereby some of the Si—O bonds are broken and an irregular network of



is formed. Further distortion of the network is obtained by introducing alkali and alkaline earth metals into the lattice. If fluorine is included in the frit, more bonds are broken; in this case an oxygen atom (—O—) linking two silicon or boron atoms is replaced by a fluorine atom (F—) which being monovalent cannot joint two Si or B atoms, hence causing bond rupture. A study of the relevant phase diagrams and eutectics proves useful in formulating low firing enamels.

Thus all frit ingredients act as either network formers or modifiers and with the principal exception of silica, titania and zirconia, all cause a diminution in acid resistance. The reacting acid causes an exchange between metal ions in the network modifier of the glass and hydrogen ions from the acid. This naturally occurs at the enamel surface, but as the etching or leaching reaction proceeds, a resulting thin layer of silica-rich material inhibits further reaction. Thus acid attack is dependent upon enamel composition and pH, with time and temperature playing a part. Sodium oxide and boric acid are both leached out by acid attack, and it has been found that the $\text{Na}_2\text{O/B}_2\text{O}_3$ ratio is constant for any one enamel and is dependent upon enamel composition.

An increase in titania content of the frit acts in a similar way to increasing silica in enhancing acid resistance with the added advantage that the coefficient of expansion is also raised slightly and the glass viscosity not increased as much as by the equivalent SiO_2 increment. This only applies to the titania remaining in solution in the glass and does not necessarily hold when the frit is supersaturated with TiO_2 , which occurs with the modern opaque sheet iron covercoats when some of the pigment recrystallises and causes opacification on cooling from the firing process.

In formulating holloware enamels the degree of acid resistance required is less than for chemical plant, e.g. reaction vessels, and consequently the RO_2 (SiO_2 and TiO_2) is lower thus permitting increased quantities of fluxes to be incorporated which confer improved 'workability'. Furthermore, they can be fired at lower temperatures and have superior chip resistance. Conversely, chemical plant enamels are higher in silica and dissolved titania and require harder firing. An example of such an enamel is shown in Table 16.1.

The acid resistance called for on domestic appliances varies with the particular component, e.g. the oven interior of a gas cooker necessitates a higher resistance than the outside sides — the former being at least Class A using 2% sulphuric acid while the latter can have a lower grading based on the less aggressive citric acid tests. These tests are detailed in BS 1344:Part 3 (ISO 8290) and BS 1344: Part 2 (ISO 2722), respectively.

The enamel mill addition, degree of firing and furnace atmosphere all affect acid resistance. An increase in clay and alkaline electrolyte detracts from this property and underfiring also has an adverse effect. The use of organic suspending agents is thus preferable to clays, from this aspect, but

other factors must also be considered. Similarly the replacement of 1% milling clay by $\frac{1}{4}\%$ of the more colloidal bentonite is beneficial. Large additions of quartz at the mill improve heat resistance and, provided the firing temperature is increased to dissolve a sufficient quantity of this silica in the glass, the acid resistance is also enhanced.

In the glass-bottle industry the bottles can be cooled in a dilute SO_2/SO_3 atmosphere to increase chemical resistance. A similar effect has been noted with vitreous enamel. It has been postulated that a thin layer of $-\text{OH}$ groups or $-\text{OH}-\text{H}_2\text{O}$ (hydronium) ions is adsorbed on the surface of a fired enamel. These ions are transformed into $-\text{OSO}_2$ or $-\text{OSO}_3$ in the presence of oxides of sulphur which are more resistant to further acid attack. It is known that the acid resistance of a recently fired enamel improves on ageing, probably due to the enamel reaction with SO_2/SO_3 in the atmosphere and it is quite common for the grading to improve from Class A to Class AA (BS 1344).

In enamels for chemical plant such as autoclaves it is not only the degree of acid resistance which is important but also the freedom of the finish from minute flaws detectable by high frequency spark testing or chemical methods. The chemical methods depend upon a colour change when the reagent such as ammonium thiocyanate reacts with the iron exposed at the bottom of the pinhole or flaw in the finish. Alternatively, an electric cell can be formed via the exposed iron in the flaw and detected chemically.

In general, strong mineral acids are more severe in their attack on enamel than weak organic acids. Vargin³ has stated that the severity of action of organic acids on enamel increases with the increase in the dissociation constant of the acid. Temperature plays a major part in acid resistance, the nearer the boiling point the greater the rate of attack. It is more significant than acid concentration.

It is recognised that vitreous enamel possesses good acid resistance, but an exception occurs with hydrofluoric acid. This is due to the relative ease of reaction between this acid and the silica (which is the largest constituent in the frit) to form silicon tetrafluoride. This reaction is made use of in some 'de-enamelling' plants.

Alkali and detergent resistance The usual method of de-enamelling sheet iron is by immersion in fused or hot strong aqueous solutions of caustic soda when the silica network is broken down to form sodium silicate. However, in spite of this fact, enamels are capable of withstanding detergents and mild alkalis and this finish is often used very successfully in washing machines, baths, sink units, etc. where alkaline conditions prevail. Such enamels are usually higher in alumina than acid-resisting enamels and often contain zirconia in the frit. Other elements which aid alkali resistance are barium, calcium, lead and zinc and their function in this context is to increase the bond with the essentially silica network and form insoluble silicates which act as a protective coating slowing down the formation of soluble sodium silicate. The necessity for alkali resistance is relatively limited when compared with detergent resistance and it has been shown that whilst these two properties are similar, a finish resistant to one is not necessarily as resistant to the other.

The Institute of Vitreous Enamellers produced a report on detergent

resistance in 1959⁵ and the following facts are taken from it:

1. Semi-opaque acid-resistant titania enamels and alkali-resistant frit generally have good detergent resistance whereas non-acid-resistant sign enamels and $\text{Al}_2\text{O}_3/\text{B}_2\text{O}_3/\text{P}_2\text{O}_5$ -based finishes have poor resistance.
2. Initially, detergent attack is accompanied by a deposit on the enamel surface which can be abraded off resulting in an apparently unaffected glossy appearance. This contrasts with acid attack when a progressive weight loss occurs and original gloss cannot be restored once it has been lost or diminished. After more prolonged detergent attack it is not possible to restore the original high gloss.
3. The rate of attack is very dependent upon temperature, that at boiling being several times greater than that at room temperature.
4. An increase in milling clay has a marked effect on improving this property.
5. Increased detergent concentration, coarser grinding of the frit and non-standard firing all cause minor deterioration in resistance.

In the design of an enamel for a washing machine tub, detergent resistance alone is not sufficient and the enamel must also be capable of withstanding the possible abrasive action of buttons, zip fasteners, etc.

Resistance to water and atmosphere These properties are of particular importance in enamelled signs, architectural panels, cooking utensils and hospital ware subjected to repeated sterilisation. That such enamelled signs as 'Stephen's Inks', etc. are still in existence and in good condition after many years outside exposure coupled with the fact that the use of vitreous enamel as a finish for architectural panels is growing are ready pointers to the good water and atmospheric resistance of enamel. Enamelled hospital utensils such as kidney bowls score over organic finishes because of their ease of sterilisation and also because they are less accommodating to germs, bacteria, etc. on account of their lower electrostatic type attraction for such microbes.

The action of water on enamel is in many ways similar to that of acids in that the network modifier is the weak link and through hydrolysis can be removed from the glass system resulting in loss of gloss and a porous surface. As with acids and alkalis, the attack on the glass by water can be continued in extreme cases, by an attack on the inorganic colouring matter initially liberated or made more active. In an enclosed system the soluble salts first leached out from the enamel by water become in turn the corrosive element and further attack is dependent upon the pH of such a salt, or, for example, on the $\text{Na}_2\text{O}/\text{B}_2\text{O}_3$ ratio.

The introduction of divalent calcium and barium oxides into frits in preference to monovalent sodium and potassium generally increases water resistance. Furthermore, oxides of tetravalent and pentavalent metals have a favourable effect on the resistance of glasses and enamels to water. The influence of B_2O_3 and fluorine in the frit upon chemical resistance is variable and is dependent upon the content of them and the balance of the frit constituents, but they usually cause a diminution in resistance. In general, mill-added clay, silica and opacifier increase water resistance provided the firing or fusing of the enamel is at the optimum.

As is expected, atmospheric resistance is related to water and the acid formed from CO_2 , SO_2 , SO_3 , etc. The action of ultraviolet light has no apparent effect on vitreous enamel unlike the case with organic finishes.

There is good correlation between atmospheric resistance and acid resistance, and this fact is helpful to manufacturers of architectural panels who can easily and quickly determine the latter property and not have to carry out lengthy exposures to the relatively unpolluted air. An exception, however, occurs with reds and yellows where a strict correlation is not always true, and in these cases a test based upon exposure to a saturated copper sulphate solution under illumination by a white fluorescent light has been advocated.

In the main the comments recorded in this section apply to enamels fused onto sheet and cast iron. Enamel is, however, applied to aluminium, stainless steel, copper and noble metals on account of its aesthetic value and also to confer durability to the base metal. With low melting point metals such as aluminium it is obvious that superb resistance to chemicals is not so feasible as if iron was the base. Nevertheless, such metals are vitreous enamelled in growing quantities and sold, indicating that the range of colour and durability obtained is superior to that possible with alternative finishes.

It can justly be claimed that a vitreous enamel coating applied to sheet or cast iron (or indeed any other metal) will confer to the basic shape colour, gloss, texture and a high degree of resistance to corrosive influences.

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16.2 Thermoplastics

Introduction

There has been considerable growth in the use of thermoplastics as corrosion-resistant coatings in the last 30 years. In the 1950s a few hundred tons per year were being applied by techniques such as fluid-bed coating, plastisol dipping and solution spraying. Since then a large number of other metal finishing technologies have been introduced, including coil coating and extrusion coating. The current tonnage of thermoplastics used in Europe must by now be some tens of thousands of tons.

Thermoplastics which are used for corrosion protection can be applied in coatings as thin as 0.025 mm by solution techniques and in excess of 5 mm by extrusion or plastisol dipping. They are used where environmental resistance, chemical resistance, abrasion resistance, sound deadening or cushioning are required. They are used in those market areas that necessitate metallic mechanical strength plus thermoplastic corrosion resistance.

Substrate Preparation

Whatever application method is used, the maximum corrosion resistance can only be achieved if the metalwork is properly prepared. This preparation consists of dressing, blasting and conversion coating.

Dressing Sharp edges must be removed. Thermoplastics have a greater coefficient of thermal expansion than metals. They therefore shrink onto the metal and if sharp edges are present then these will cut through the coating and become exposed. These exposed edges will start to corrode and this will inevitably result in underfilm creep corrosion.

Welds should be continuous and porous-free and dressed to remove lumps and weld spatter.

Degreasing Mild steel is generally given a temporary protective coating of oil which must be removed. This is done in a vapour degrease tank using chlorinated solvents such as 1,1,1-trichloroethane or trichloroethylene. Alternatively, an aqueous alkaline degreasing solution can be used. It is beneficial to use the former prior to grit blasting and the latter prior to conversion coating.

Shot or grit blasting Blasting is used to remove rust and to increase the surface area and hence increase apparent adhesion. A variety of abrasives is available, including chilled iron grit and aluminium oxide. The selected abrasive is fired under pressure at the metalwork to create the desired result.

Conversion coating Conversion coatings are chemical solutions which react with the metal surface to create a corrosion-resistant layer onto which the coating can bond. For mild steel iron phosphate is used to attain good adhesion, but it does not give the underfilm corrosion resistance which can be obtained using zinc phosphate. Zinc coatings can be treated with either zinc phosphate or chromate. Aluminium is usually treated with chromate^{2,3}.

Application Methods

The application methods will be categorised by the physical form of the thermoplastic, e.g. liquid, powder, granule.

Liquid Application Methods

Spraying Thermoplastics solutions such as those based on p.v.c./p.v.a. copolymers may be applied by conventional paint spraying equipment. Because they are thermoplastic they do not require heat to crosslink them, but they may require some heat to evaporate off the solvents.

When the solubility of the thermoplastic is poor at room temperature it may be possible to produce a dispersion in a mixture of diluents and latent solvents. This dispersion may be applied by conventional paint spray equipment. The coated item is placed in an oven where the diluents evaporate off. The latent solvents then dissolve the thermoplastic and evaporate from this solution at a controlled rate, thus producing a continuous film. P.V.F., and p.v.d.f. and p.t.f.c.e. coatings are produced from dispersions of this type.

Solvent-free p.v.c. plastisol may be spray applied. P.V.C. spray coatings are currently used extensively by the automotive industry for undersealing of vehicles to prevent corrosion. The plastisol, being resilient, is not cracked or abraded by stone chippings. P.V.C. plastisols have a high viscosity compared with solution and other dispersion systems. Therefore, they have to be applied by airless spray or air-assisted airless spray equipment. P.V.C. coatings must be heated to produce a solid tough coating on cooling. The reasons for this are discussed later in the materials section.

Dipping P.V.C. plastisols are used for corrosion protection of pipes, tanks etc. against aqueous chemicals and slurries at temperatures up to 60°C. They are used for the coating of plating jigs to prevent the jigs from being plated and also to prevent corrosion caused by the various acid etching solutions used in the plating process.

The coating technique starts by applying a solvent-based adhesive on to a previously pretreated metal substrate. The item is then preheated to 200–250°C, the exact time and temperature depending on the metal thickness. It is then dipped in the plastisol which partly gels owing to the

heat radiating from the item. It is then raised out of the plastisol and placed in an oven for final gelation, when, its optimum physical properties and full chemical resistance will be attained.

Coil coating Coil coating is the technique of depositing a film of liquid on to a continuously moving thin steel or aluminium sheet. The sheet is uncoiled from a roll at the start of the process and recoiled at the end. The coils are then cut to length and formed into the required shape.

During the process the sheet will pass through pretreatment tanks. It is coated with adhesive primers and top coats. Stoving is usually necessary after application of each coat. When p.v.c. is applied at thicknesses in excess of $100\text{ }\mu\text{m}$ the coating can be embossed to produce a variety of textured finishes, for example a leather grain effect. The coil coating industry in Europe is using about 50 000 t of paint per year. This figure includes a significant quantity (between 5 000–10 000 t) of p.v.c. applied as plastisol and some p.v.d.f. applied from a dispersion.

P.V.C. is used extensively in the building industry for external cladding and internal partitions. It is used because it has excellent weathering properties and will protect the substrate against corrosion for periods in excess of 10 years. When it is applied at a thicknesses of about $200\text{ }\mu\text{m}$ it can withstand the hard handling techniques often associated with building sites.

P.V.D.F. is used where very high UV resistance is required, e.g. external building cladding in tropical countries.

Powder Application Methods

Thermoplastics can be produced in the form of a powder by grinding extrusion-compounded granules. The grinding can be carried out at ambient temperature when rotating blade or rotating disc mills are used. Alternatively, those thermoplastics which are heat sensitive or very tough at ambient temperature may be cryogenically ground on a pin-disc mill. Whichever technique is employed, the correct particle size distribution is obtained either by the use of an air classifier or by conventional screen mesh sieving.

Fluidised bed The fluidised bed consists of two boxes on top of one another. The top and larger one contains the powder, and the lower one is separated from it by metal mesh and a semipermeable membrane. Air is pumped under pressure into the lower compartment and then diffuses through the membrane and through the powder. The powder particles are lifted and separated by the air. This results in a considerable reduction in the bulk density so that the item to be coated can easily be submerged in the powder.

The pretreated metalwork to be coated is heated in an oven to a temperature of between 260 and 360°C , depending on the metal thicknesses and the coating to be applied. It is then withdrawn from the oven and dipped into the fluidised powder. Here the fine powder particles are blown onto the hot metal where they melt. After a few seconds (5–10s is normal), the item is removed from the powder and the unfused outer particles are allowed to fuse. Then either the item is allowed to air cool or it is water quenched. The cooling method can affect crystal structure and hence surface finish and

physical properties. If there is insufficient heat content in the metal further heating may be necessary to fuse the coating fully and produce an acceptable surface finish.

The fluidised bed coating technique is used extensively for wirework items such as dish drainer racks, vegetable racks, office trays etc. The technique is also widely used for street furniture e.g. metal lampposts, signposts and balustrading, and for metal office furniture and domestic garden furniture. It also provides chemical corrosion resistance on valves, pipes, couplings etc.

Plastics used for fluidised bed powder coatings include polyethylene, p.v.c., nylon, p.v.f.2, p.e.c.t.f.e. and a variety of polyolefins and their copolymers.

Electrostatic powder spraying In the electrostatic powder spraying process plastic powder is blown under pressure from a hopper through a gun. The gun has a barrel 15–45 cm long and 3–5 cm in diameter. At the end of the gun is a charged point. The charge is between 10 and 20 kv and may be positive or negative. The powder picks up the charge and is attracted to the pretreated metal object which is earthed. The item is then placed in an oven to fuse the powder into a smooth coating. The powder particle size should be 20–75 μm . Particles smaller than 20 μm are too light to be transported by the compressed air and form a charged cloud through which further powder does not pass easily. If particles are too large, the charge-to-mass ratio is too low and the particles tend to fall before reaching the earthed metal item.

Most thermoplastics are not suitable for spraying because they are too tough. If they were brittle enough to be economically ground to the required fine particle size the physical properties of the coating would be poor. Also, for optimum charge retention the volume resistivity of the powder should be at least 10^{-13} . Most thermoplastics fall below this. However, Nylon 11 powders are available for general use and p.v.c. powders are used for coating continuous galvanised wire mesh for fencing.

Guns have been developed that generate the electrostatic charge by friction rather than by electric high voltage. These are the turbo-electric guns. Their advantage over the electric type is safety. Their disadvantage is lack of control.

Flame spraying In flame spraying applications the pretreated items should be heated by passing the flame gently over the metal surface. A skin temperature of 60–100°C is usually sufficient. This ensures that the molten droplets will flow out and fuse together to give a smooth finish with good adhesion to the substrate. The powder is then blown through a very hot flame, melts and is deposited as molten droplets onto the item to be coated. The gases used to produce the flame should not produce an oxidising atmosphere since this will dramatically reduce the physical and chemical resistant properties of any thermoplastic applied.

The particle size of the powder should be 150–300 μm . If the particles are too big they will not completely melt and a poor surface finish will result. The flame will inevitably cause some degradation to the surface of the particles. Since the surface area to mass ratio increases as the particle size decreases, very fine particles should be avoided.

The process is not widely used in factories but has found a niche in coating large external structures, e.g. large security gates. It can also be used for the

repair of coatings which have suffered on-site damage.

The major concern with this technique is that the polymer will be degraded by the very high temperatures employed. In addition, the process is very operator dependant. To become, more acceptable, a great deal more work needs to be done in equipment design and material technology.

Cascade coating The cascade coating technique is used extensively for the external coating of metal pipes with polyethylene to convey natural gas throughout Europe. There are several ways of using this technique but in all cases the pipe is evenly heated to a surface temperature of 250–350°C. Powder is then poured from above, 'cascaded', onto the rotating pipe. A second heating operation may be necessary to completely fuse the powder.

There are two common variants of the coating method. In the first, the complete length of pipe is heated either in an oven or over a bank of gas burners. The pipe is then moved to an area where the powder is cascaded on to the rotating pipe from a hopper which extends the full length of the pipe. The excess powder is collected in a trough below and recirculated to the hopper. In the second method the pipe rotates and moves laterally through a bank of gas burners or an induction heater, then through a continuous, but narrow, cascade of powder. The cascade comes from a hopper which is at right angles to the direction of movement of the pipe. The pipe continues to travel through a second bank of gas burners where complete fusion of the powder takes place.

The coating is applied to protect the steel from corrosion due to the acid or alkaline condition of the soil surrounding the pipe in service. Usually, the process requires three layers. First, an epoxy powder is applied to achieve adhesion to the pretreated metal and therefore resistance to cathodic disbondment. Second, a 'tie' layer of polyolefin copolymer is applied and third a thick layer of polyethylene is cascaded, which in effect protects the epoxy from physical damage.

Rotational lining The rotational lining technique is derived from the rotational moulding technique, the mould being replaced by the item to be coated. The technique may be used for coating the inside of all kinds of cylinders and has found particular favour among the makers of fire extinguishers. A special self-adhesive stress crack-resistant grade of polyolefin is used in the majority of water-based fire extinguishers in the UK.

The rotational lining technique consists of pouring a predetermined weight of polymer powder into the preheated cylinder. The cylinder is then rotated in two perpendicular axis while the outside of the cylinder is heated. The heat may be from direct radiant burners or the complete rig may be positioned in an oven. The item must be rotated during the cooling cycle to prevent sagging. To reduce the possibility of polymer degradation and to optimise cycle time, it is essential that the powder is heated to the minimum temperature that will ensure the production of a porous-free, uniformly thick, coating inside the cylinder.

Miscellaneous powder coating methods Apart from the coating techniques described briefly above, the jobbing or custom coater has a whole armoury of other methods which are more or less related to those described above.

Channelling This technique is used for coating the inside of a pipe. The pipe, which is continuously rotated, is heated over a bank of heaters stretching the length of the pipe. The required amount of thermoplastic powder is weighed and put into a metal channel. The channel is then put inside the pipe, inverted to empty it, and withdrawn. The skill is in removing the channel without badly scoring the coated surface. When full fusion of the powder has occurred, the heat is turned off and the pipe continues to rotate until the coating has solidified.

Flock spraying This technique is used where electrostatic spraying is inappropriate, e.g. where thick coatings are required. The pretreated metal is heated and the powder is blown onto the workpiece from a flocking gun which is similar to a conventional wet paint gun but with no needle and with the nozzle 1–2.5 cm in diameter. The metal should be preheated to a temperature sufficient to fuse the powder without further heating, but occasionally it may be necessary to apply a naked flame over the surface to ensure a good finish. This technique can be used for coating the flange ends of pipes which have been lined by channelling.

Granular Application Methods

The two major plastics processing techniques of extrusion and injection moulding are used for coating metals.

Extrusion In very simple terms the extruder is a heated cylinder containing a rotating screw. There is a hopper at one end to supply the plastic granules and a die at the other through which the molten polymer is extruded. The technique is widely used for producing garden hose, automotive trim, window profiles, plastic films etc. But it is also used for the corrosion protection of metal tube, rod and wire. Fencing wire is coated in PVC using this technique. The wire may then be woven into chainlink mesh fencing. However, there is normally no adhesion between the coating and the wire. Adhesion can be achieved if the fluidised bed process is used.

Injection moulding The injection moulder is a machine which first melts a thermoplastic and then injects that molten polymer into a mould. Such items as baskets, bowls, bins, telephones and electronic housings are produced by this technique. It can be used for lining valves. In this case the valve would be used as part of the mould. Very thick coatings are produced which give chemical resistance to the valve. At the same time, the metal valve housing will protect the valve from mechanical damage.

The polymers used for this process include polyethylene, polypropylene and p.v.d.f.

Materials

Liquids

PVC/PVA copolymer solutions Polyvinyl chloride/polyvinyl acetate copolymers can be readily dissolved in blends of aromatic hydrocarbon,

ketone and ester solvents to produce *solution vinyls*. Terpolymers containing acid groups can be blended with the copolymer to enhance adhesion to metal substrates. Plasticisers can be added to improve flexibility and conventional p.v.c. stabilisers are used where thermal or UV resistance is required.

They are applied by wet paint spray techniques and have the advantage, over other paint systems, of long-term flexibility. Conventional alkyd systems may have an initial degree of flexibility, but within 12 months outside become rigid and then crack due to thermal expansion and contraction of the substrate. This phenomenon is less likely to occur with a well formulated vinyl solution.

P.V.D.F. Polyvinylidene fluoride (p.v.d.f. or p.v.f.2) dispersions are applied by the coil-coating process. They are blends of p.v.d.f. resin and acrylic. The combination produces a system which has excellent weatherability and which can be bonded via an adhesive primer to a galvanised steel or aluminium substrate.

They are used where prolonged exposure to high UV resistance is required, such as prestige building cladding in tropical and sub-tropical climates.

P.V.C. plastisols P.V.C. plastisols are liquids which contain little or no solvent/diluent. They consist of a blend of polyvinyl chloride (p.v.c.) resins, plasticisers, stabilisers, viscosity depressants, pigments and sometimes fillers.

Whatever application method is used, there is always a heating step. When p.v.c. plastisol is heated to over 100°C the p.v.c. resin which is suspended in plasticiser stabiliser etc. starts to dissolve in the plasticisers. When solution is complete the system is cooled to room temperature and a solid homogeneous coating results.

The thermal and UV resistance will depend on the stabiliser systems used. The hardness of the coating will depend on the amount and type of plasticiser used. Correct selection of the plasticiser can permit the use of the plastisols at high or low temperatures, provide fire resistance or oil resistance. Plastisols can be produced in a range of gloss levels from 80 units down to 10 gloss units.

The application method used depends on the intended use of the item. *Spraying* is used by the automotive industry to underseal the substructure of vehicles to provide corrosion resistance. Plastisol coatings are tough enough to resist mechanical damage from stones and other objects thrown up from roads. *Coil coating* is used to coat galvanised steel sheet. The building construction industry uses this for the exterior cladding and roofing of buildings. Lifetimes of 15 years and more can be expected before first maintenance. Internal partitioning is produced by the same process. Shelving and electronic equipment housing are also produced from coil coated steels.

Dipping is used to apply coatings of 1–6 mm thick to pipes, tanks, vessels, etc. in a wide range of uses:

1. water cooling pipework in power stations;
2. pipes, tanks, extraction hoods and ducting in the chemical industry for many acid, alkaline and neutral solutions up to 60°C;
3. pipework in the water section of oil/water separation plants on offshore oil platforms;

4. hoppers and stillages to reduce noise and damage to components in the engineering industry.

Powders

Polyethylene Polyethylene is one of the lowest cost thermoplastic materials. Hence when looking for a coating or lining it is generally considered first.

Three types of polyethylene are available:

1. Low density polyethylene produced by a high-pressure high-temperature reaction process. This creates a molecule with a high degree of random branching. Thus crystallinity and hence density are low.
2. High density polyethylene produced by a low-pressure low-temperature process involving Ziegler-Natta catalysts. This creates low levels of branching and hence a high degree of crystallinity.
3. Linear low density polyethylene is also produced by the low-pressure low-temperature Ziegler-Natta catalyst route. Other monomers are incorporated such as butene or octene, which disrupt the crystallinity and reduce density.

All polyethylenes are soft, flexible and resistant to acids and alkalis up to 60°C. They retain this flexibility down to -40°C. Hence they have good resistance to impact even at low temperatures. However, unless correctly formulated they can suffer from environmental stress cracking (ESC), poor adhesion and UV degradation. ESC is the phenomenon which occurs when a thermoplastic is put under stress, e.g. bent, in a particular environment and prematurely cracks or crazes. Alcohol and detergent are examples of agents that can cause ESC in polyethylenes.

Fluidised bed coating Unmodified polyethylenes are used for coating wire-work items such as vegetable racks, record racks etc. Light stabilised grades are used for coating garden wirework such as compost bins or hanging baskets. Highly modified systems containing adhesion promoters are used for chemical resistant applications such as coating pipes, valves, etc.

Polyolefin copolymers Although there is a wide variety of these available, the only one currently commercially available as a compounded powder is saponified EVA. This is reported to have good weatherability and will not suffer from ESC. One major advantage this coating has is that it can be applied by the fluidised bed process at low temperatures and this offers the possibility of coating temperature-sensitive metals such as galvanised steel.

Polyolefin alloys Plascoat Systems Ltd. has developed a range of polyolefin alloys in its Performance Polymer Alloy (PPA) range. The exact compositions of these are secret. These products have been tailor-made to meet the needs of specific markets, e.g.

- (a) Lining the inside of aqueous-based fire extinguishers. This requires a coating material which will adhere to the inside of the fire extinguisher. It is applied by a rotational lining technique and must not melt and sag

during the curing of the epoxy powder paint used on the outside. Furthermore, it must not suffer from stress cracking in service.

- (b) The lining of hot water cylinders. This requires a coating which will adhere well to metal. It must have good resistance to water at 80°C and be largely impermeable to water to prevent corrosion of the metal substrate.
- (c) Coating of bus-bars. The coating must have excellent electrical resistance. It must be capable of being applied at thicknesses of up to 2 mm. In this case there is no adhesion so that the coating can easily be stripped off to allow contacts to be made after installation if necessary.

P.V.C. P.V.C. powders are blends of p.v.c. resin, plasticisers, stabilisers and pigments. The plasticisers soften the coating and increase impact strength. The amount normally used in p.v.c. powder creates a coating with a Shore A hardness of 80–90 units. With this level of hardness the coating will be resistant to impact damage down to –5°C and at the same time will not be so soft as to significantly affect resistance to impact penetration at higher temperatures.

The stabilisers are selected to give adequate thermal stability during processing and excellent UV resistance in service. Correct plasticiser selection can decrease the water permeability of the coating and increase the long-term adhesion and hence corrosion resistance. The pigments are present to give aesthetic appeal, but they must be correctly selected for optimum resistance to the effects of weathering.

After metal pretreatment it is essential that a suitably formulated adhesive primer is used, because p.v.c. does not itself adhere to metals.

Fluidised coating In the UK p.v.c. powders are widely used for coating street furniture and fencing posts. Street furniture includes road signposts and brackets, lampposts, balustrading and seating. In the UK and the rest of Europe p.v.c. coatings are used for welded wire mesh used for fencing. In the USA p.v.c. (vinyl) is a general coating material and is used for coating, for example, dishwasher baskets.

Electrostatic spraying PVC can be applied by the electrostatic process to continuous galvanised wire mesh.

Nylon 11 Nylon 11 is a hard abrasion-resistant, scuff-resistant coating. When correctly formulated and applied, it can be used for exterior application. It has good resistance to solvents and to a range of alkalis and salt solutions up to 80°C. If water quenched, the coating has excellent impact strength. However, Nylon 11 is crystalline and pull-back from sharp edges can be a problem. It is therefore essential that metal work is well radiused.

Nylon 11 is applied using a fluidised bed process to a wide variety of substrates including metal chair frames, door furniture and wire dishwasher baskets. It can also be applied by electrostatic spraying, but generally only where the application is decorative and where the metal work is thin, i.e. less than 0.2 mm.

P.V.D.F. Polyvinylidene difluoride is a coating which offers resistance to

Table 16.4 Properties of thermoplastic powder coatings

<i>Property</i>		<i>Polyethylene</i>	<i>Polyolefin copolymer</i>	<i>Polyolefin PPA 65 alloys</i>	<i>P. V. C.</i>	<i>Nylon</i>	<i>P. V. D. F.</i>
Relative density	(g/cm ³)	0.93	0.33	1.03	1.26	1.04	1.78
Impact strength	(J)	2	—	1.32	1.7	4.5	—
Tensile strength	(MPa)	10.3	13	13	17	40	51
Hardness	(Shore A)	70	95	95	85	98	99
Abrasion Taber (H18 load 500 g)	(mg/1 000 cycles)	415	—	210	50	33	—
External weathering		Poor*	Good	Poor	Excellent	Good	Excellent
Chemical resistance							
Acid		Fair	Fair	Good	Good	Poor	Excellent
Alkali		Fair	Good	Good	Fair	Good	Excellent
Solvent		Poor	Poor	Poor	Poor	Good	Fair

chemicals up to 90°C. It is more resistant to stronger acids and alkalis than the above-mentioned coating materials. It is also a hard abrasion-resistant coating.

It is applied using a fluidised bed process, generally in two coats. A precompounded blend of p.v.d.f., corrosion-inhibitive pigments and adhesive components is applied first, followed by a top coat of pure p.v.d.f. The primer coat protects the metal and the top coat protects the primer coat from attack by the chemicals.

The properties of the thermoplastic powder coatings are summarised in Table 16.4.

Granules

The range of thermoplastic materials that can be extruded or injection moulded is too large and varied for coverage in this book.

W. G. O'DONNELL

16.3 Temporary Protectives

Definition

Many metal articles have to be transported and stored, sometimes for long periods, and are then used with their working surfaces in the bare state. Unless these surfaces are protected between manufacture and use, most of them will rust and corrode due to the effect of humidity or atmospheric pollution. The materials used for such protection are called temporary protectives as they provide protection primarily for the transportation and storage period. The significance of the term *temporary* lies not in the duration of the efficacy of the protective, but in the fact that it can easily be removed, so that the protected surfaces, can if necessary, be restored to their original state. They provide a water and oxygen-resistant barrier by reason of their blanketing effect and/or because of the presence of naturally occurring or added inhibitors which form an adsorbed layer on the metal surface.

Types of Temporary Protectives

There are many temporary protectives on the market and it would be impracticable to describe them individually. However, they may be classified according to the type of film formed, i.e. soft film, hard film and oil film; the soft film may be further sub-divided into solvent-deposited thin film, hot-dip thick film, smearing and slushing types. All these types are removable with common petroleum solvents. There are also strippable types based on plastics (deposited by hot dipping or from solvents) or rubber latex (deposited from emulsions); these do not adhere to the metal surfaces and are removed by peeling. In addition there are volatile corrosion inhibitors (V.C.I.) consisting of substances, the vapour from which inhibits corrosion of ferrous metals.

Soft-film Materials

Those deposited in the cold from a solvent usually consist of lanolin or petrolatum mixtures in such solvents as white spirit or coal tar naphtha. The film is thinner than other soft films deposited by different methods.

Materials applied by dipping the article to be protected in the hot molten material are usually based on petrolatum. Corrosion prevention depends largely on the barrier provided by the film, but for improved protection, corrosion inhibitors are added. The film may be relatively hard and waxy or quite soft like pharmaceutical petroleum jelly.

The smearing types of material are usually lubricating grease compositions, i.e. blends of soaps and lubricating oil, but may be mixtures containing petrolatum, oil, lanolin or fatty material. They are softer than the hot-dip materials to permit cold application by smearing.

The slushing compounds are a variant of the smearing types, and possess some flow properties at room temperature so that brush marks produced during application are reduced. Some materials contain solvent, so that they are free-flowing as applied, but stiffen when the solvent evaporates.

Hard-film Materials

These were developed to facilitate handling after treatment and to avoid contamination of adjacent components. The films are deposited in the cold and should be tough and neither sticky nor brittle. The deposited films may be plasticised resins, bitumens, etc. which are varied according to the subsidiary properties required, such as transparency and colour. The solvents used vary according to the solubility of the ingredients, drying time requirements, flammability and permissible toxicity in given circumstances. As with the soft-film solvent-deposited materials, the surface coverage is large, and for this reason, and because they can be applied at room temperature, hard and soft-film solvent-deposited protectives are widely used.

Oil-type Materials

These are usually mineral oils of medium or low viscosity, which contain specific corrosion inhibitors and anti-oxidants. In spite of the relatively low protective properties of the fluid films, which are not nearly so great as those of the previously described solid films, these materials have an established field of use on the internal surfaces of tanks and assembled mechanisms, and where solid material or solvent cannot be tolerated.

Strippable Coatings

The most important of these to date are those applied by hot dipping. Many are based on ethyl cellulose and the dipping temperature is comparatively high (about 190°C). They rely mainly on the thickness (≈ 2 mm) and toughness of the coatings for their extremely good protective properties, and they have the added advantage of giving protection against mechanical damage so that little added packaging is required for transport. Re-use of the material is frequently possible. The disadvantages are the necessity for special dipping tanks and cost; this latter may, however, be offset by saving in packaging materials.

The strippable films deposited from solvents in the cold are much thinner (≈ 0.05 – 0.25 mm) than those from the hot-dip materials, and their protective properties are not nearly so good. A possible difficulty which must be watched for is the development of brittleness on ageing and consequent difficulty of stripping. Latex films containing inhibitors such as sodium benzoate have been found to deteriorate under tropical conditions, but may have a use in more temperate climates.

Special Modifications of the Aforementioned Types

These have been developed for special uses. For example, since petroleum-based materials harm natural rubber, a grease based on castor oil and lead stearate is available for use on the steel parts of rubber bushes, engine mountings, hydraulic equipment components, etc. (but not on copper or cadmium alloys). Some soft-film solvent-deposited materials have water-displacing properties and are designed for use on surfaces which cannot be dried properly, e.g. water-spaces of internal combustion engines and the cylinders or valve chests of steam engines.

A recent application of this type of fluid is assistance in the removal of ingested salt spray from jet aircraft compressors and the neutralisation of corrosive effects. Other types of water-displacing fluids are claimed to have fingerprint neutralising properties or to be suitable for use on electrical equipment. Some oil-type materials serve temporarily as engine lubricants and contain suitable inhibitors to combat the corrosive products of combustion encountered in gasoline engines.

Volatile corrosion inhibitors (see also Section 17.1) are a special type of protective, which when present as a vapour inhibit the rusting of ferrous metals. They are generally used as an impregnant or coating on paper or synthetic film; as a powder, either loose or in a porous container; or in the form of a 5% w/v solution in non-aqueous solution (e.g. methylated spirits) with application by either swab or spray. Their effectiveness in preventing corrosion depends not only upon the inherent activity of the material but also upon their volatility and rate of release from the supporting medium. Being volatile, some form of enclosure is necessary for continued effectiveness whether it is the closing of orifices with bungs or overwraps when protecting internal surfaces, or by sealing the outer container for other packed stores. Volatile corrosion inhibitors should be used with caution in the presence of non-ferrous metals which may be attacked, particularly in the presence of free water. Care should also be taken with painted surfaces and with some plastics and other organic materials which may become discoloured or damaged.

The types of temporary protectives in general use are given in Table 16.5.

General Scope of the Materials

Temporary protectives against corrosion should be used only where removal is subsequently necessary for the fitting or the working of surfaces to which they are applied.

Table 16.5 Types of temporary protectives in general use

<i>Type of protective</i>	<i>Typical ingredients*</i>	<i>Method of application</i>	<i>Properties of film</i>
Solvent-deposited hard film		Dipping, spraying, brushing	Solid, thin, tough, non-sticky, removable by wiping with solvent
(a) ordinary grade	(a) Plasticised bitumens, plasticised resins, white spirit, coal tar naphtha, chlorinated solvents		
(b) water-displacing grade	(b) As (a) above together with water-displacing agents		
Solvent-deposited soft film		Dipping, spraying, brushing	Solid, thin, greasy, removable by wiping with solvent
(a) ordinary grade	(a) Lanolin, petrolatum, with and without specific corrosion inhibitors and anti-oxidants, white spirit, coal tar naphtha, chlorinated solvents		
(b) water-displacing grade	(b) As (a) above together with water-displacing agents		
Hot-dipping soft film	Petrolatum, lanolin, with and without specific corrosion inhibitors	Dipping in molten material	Solid, thick, waxy or greasy, removable by wiping with solvent or immersing in hot oil
Smearing	Metallic soap and mineral oil, soft petrolatum, lanolin (castor oil/lead stearate for rubber-containing components)	Smearing, brushing	Solid, thick, greasy, removable by wiping with solvent

These coatings are designed to protect packaged engineering materials against corrosion due to a humid atmosphere, in both rural and general industrial conditions, during transit and storage in temperate and tropical climates. Where conditions are severe, extra packaging may be required or, in the case of thick soft-film materials, extra thicknesses may be applied. The coatings are also often used to protect unpackaged spares during shelf storage.

In normal thicknesses, temporary protectives are unsuitable for outdoor exposure and they should be protected against gross liquid water by coverings or wrappings. The petrolatum-based thick-film material and some greases, however, will give adequate protection outdoors if they are applied extra thickly. Protection cannot be expected if the surfaces remain in contact with waterlogged packing material.

Corrosion preventives should be applied to surfaces which are clean and dry or corrosion may well continue beneath the coating. Materials with

Table 16.5 (continued)

<i>Type of protective</i>	<i>Typical ingredients*</i>	<i>Method of application</i>	<i>Properties of film</i>
Slushing	Metallic soap and mineral oil, oil-softened petrolatum, lanolin, small amounts of solvent	Smearing, brushing	As for smearing protective
Oil	Mineral oil, specific corrosion inhibitors and anti-oxidants	Dipping, rinsing, spraying	Liquid, thin, oily
Strippable (a) hot-dipping grade	(a) Ethyl cellulose, cellulose acetate butyrate, mineral oil, plasticiser, resins, stabilisers	(a) Dipping in molten material	(a) Solid, tough, non-adherent, often leaves oily film with lubricating properties; film removed by stripping
(b) cold applied grade	(b) Vinyl copolymer resins, plasticisers, stabilisers-flammable or non-flammable solvents	(b) Spraying, dipping	(b) Solid, tough, non-adherent film, removed by stripping
Volatile corrosion inhibitor (V.C.I.)	Organic amino salts (e.g. dicyclohexylamine nitrite, cyclohexylamine carbonate)	From solution by spraying, as a powder by sprinkling, by wrapping with V.C.I.-impregnated paper	Adsorbed, non-visible film

*Some details of typical compositions, where these are available, are given in *Petroleum, Oils and Lubricants (POL) and Allied Products*. Defence Guide DG-12, Section IV, Ministry of Defence, H.M.S.O., London (1968).

special properties such as water displacement or the ability to neutralise fingerprints should not be used in place of drying and clean handling, but only where the application demands it.

Causes of Failure

In practice it is usually difficult to establish the reasons for failure as a number of factors may be simultaneously responsible, such as (a) application of the protective to dirty surfaces, (b) carelessness in application, (c) inherent inadequacy of the material, (d) exposure to unreasonably severe conditions, (e) inevitable difficulties in application. Point (c) includes inadequacy not only in protective properties but, in the case of the hard-film materials, in certain physical properties, e.g. the film may become brittle and flake when handled, may remain too sticky and become contaminated with dirt or adhere to the

wrapping paper more strongly than to the surface to be protected, may age to form an insoluble material and become difficult to remove, or may not remain flexible and adherent at low temperatures. Point (*d*) includes, for example, the use of soft-film materials in hot conditions at temperatures too near to their melting point. As regards (*e*), it may be difficult to avoid thin places in the film arising from contact with other surfaces during the process of application, drying-off of the solvent, or cooling; when such thinning occurs, good surface-active properties are advantageous. In this connection, it may be pointed out that scraping in transit and stacking, and local thinning due to grit, dirt, etc. are common; it follows therefore that shelf storage of unpacked items should be avoided if possible.

General Comments on Application

Application by dipping gives the most complete film, is the most economical in material, and is usually the quickest for large quantities of articles. This method should be chosen whenever possible. Spraying is the next best. Brushing and hand-smearing should be adopted only when dipping or spraying is not feasible.

During the dipping process, articles with recesses should be rotated in the bath so that air can escape. Dipping baths should be kept covered when not in use to prevent contamination, and, in the case of solvent-containing materials, to prevent concentration by evaporation of the solvent, as this would lead to excessive film thicknesses and long drying times. The composition of a bath of solvent-containing material should be checked periodically. Unaided evaporation of the solvent from solvent-deposited films is usual, but the process can be speeded up by blowing air over the articles or by gentle warming; the heating, however, should not be excessive.

During hot-dipping in petrolatum-based materials, film thickness can be varied by altering the temperature of dipping and the duration of immersion. The petrolatum will first chill on to a cold article put in the bath, the solid coating bridging small crevices. This may give sufficient protection, but it may be desirable for the article to attain the temperature of the bath so that the molten petrolatum will penetrate into all the crevices, e.g. between the ball and race of a rolling bearing. The article may then be withdrawn, allowed to cool and given a quick dip to build up the film thickness.

Choice of Temporary Protective

Hard-film protectives can be applied to most types of single articles and are especially suitable in mass-production systems. They should not be applied to assemblies because the hard film is liable to cement mating surfaces together and considerable difficulty may arise in the removal of the protective film. This type of protective should be removed before the article is put into use.

The soft-film solvent-deposited type can be used broadly for the same purposes as the hard-film type. A grease-resistant wrapping is required as an inner wrapping (as for all soft-film types) in packaging. Grades of this

material, consisting essentially of lanolin in a solvent, have been found to give better protection to packaged articles than some of the best available hard-film materials, and are to be preferred for articles with very high precision surfaces. The film is usually dispersable in lubricating oil and it is therefore not so important to remove it from surfaces when an article comes into use except when it has become contaminated with grit and dirt.

The thick soft films produced by hot dipping are suitable for highly finished as well as normal machined surfaces. Grades with drop-points substantially higher than 50°C are preferable for tropical storage as otherwise marked softening and possible thinning of the protective film is likely to occur. These films can be applied to many types of assemblies, the chief exceptions being assemblies with inaccessible interiors that cannot readily be blanked-off and fine mechanisms where any residue might interfere with the free movement of parts or their subsequent lubrication with low viscosity oil. These films can also be used on parts which might be affected by the solvent from the thin or soft film protectives, but they should not be applied to items having plastics or leather components.

Greases are usually applied by brush or smearing; the brush must be sufficiently stiff to give intimate contact with the surface yet not so stiff as to leave deep brush marks. Greases should not be melted and therefore cannot be applied by dipping or spraying; also, no attempt should be made to dissolve them in a solvent for application. They are particularly useful where only part of the surface of the item requires protection, because of the ease of application by cold smearing. They can be used in this way also in conjunction with solvent-deposited protectives for assemblies of a low degree of complexity, by coating screw threads and filling clearance spaces before dipping the article in the solvent-containing protective. Grease films can be made thick enough to give the desired level of protection. Wrapping is desirable to protect the very soft film. Removal before use is chiefly for the purpose of removing grit and dirt.

The slushing material finds its most useful application on big machinery requiring protection of large areas during storage or during intervals of idleness in machine shops. The effect of dust and dirt contamination should therefore be considered an important factor in assessing the quality of these materials.

The lower protective quality of oil-type materials largely restricts their use on internal surfaces of, for example, internal combustion engine cylinders, and gear-box and back-axle assemblies of motor vehicles. Such materials are widely used to fulfil the simultaneous function of a protective and a lubricating oil; e.g. in sewing machines the protective can also serve as a lubricant during its initial period of use. The functions of corrosion inhibitor and hydraulic oil are also often combined. Oil-type materials are also used on small nuts, screws and washers which cannot easily be protected by solid-film materials; in this case protection must be reinforced by good packaging.

The hot-dip strippable coating is applicable when a high standard of protection from corrosion and mechanical damage is required, as on gauges and tools which so often have their working surfaces facing outwards. Assemblies must have orifices plugged so that molten material cannot penetrate during the dipping.

Volatile corrosion inhibitors are particularly useful when oil, grease or other adherent films are unsuitable. They should be used in conjunction with a primary wrap which should form as close an approach to a hermetically-sealed pack as possible. They are widely used to provide protection to precision tools, moulds and dies, and also on a larger scale to car body components.

General Remarks

The listing of so many types of protective might indicate some complication in use. It should, however, be realised that the materials are to some extent interchangeable, and in most works it is seldom necessary to have more than two or three materials. It is emphasised that protection should be given by the manufacturer of the article as soon as possible after its fabrication; if stocks have to be held in a part-finished state, protection should also be given during this period. This is important for cast iron because corrosion once started is difficult to stop. If the conditions at the receiver's works or depot are particularly severe, the maker's protective processes should be appropriately supplemented.

The bibliography given below is classified according to the aspect of the subject mainly dealt with, but some references, of course, deal with several aspects. In addition there is a considerable body of patent literature concerning specific inhibitors.

Recent Developments

Strippable coatings based on such resins as vinyl, acrylic and polyethylene are finding increasing favour for applying to finished products to protect them during transit, the coating being left on the product until it reaches the dealers showroom or, in some cases, the consumer. These coatings offer excellent temporary protection against moisture, chemicals and weathering and some stand up well to such fabricating techniques as bending and deep forming. The coatings are easy to apply and some remove simply by piercing the film and peeling it off, others by washing away by applying an alkaline solution or solvent.

The toxicity of lead-containing greases has led to alternative products being used for the protection of components where the product is likely to come in contact with rubber. Of those products considered silicone-based greases have been found to be particularly suitable and their application to hydraulic equipment components such as brake cylinders, where they can provide internal protection against corrosion both during transit and use, has been found particularly beneficial.

Corrosion-inhibited petroleum-based waxes deposited from solvent are finding application in both the automotive and aircraft industries for the supplementary protection of hollow sections of the finished product. These waxes are applied by airless or air-assisted pressure-feed spraying techniques

to clean and dry, but often painted, surfaces to provide increased protection against corrosion due to humid and corrosive atmospheres during both transit and use.

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17 CONDITIONING THE ENVIRONMENT

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17.1 Conditioning the Atmosphere to Reduce Corrosion

The impurities normally present in uncontrolled atmospheres are capable of producing serious corrosion on many metals and alloys which do not corrode significantly in clean, dry air (Section 2.2). It is therefore in principle possible to prevent corrosion by purifying the atmosphere, or by using a volatile corrosion inhibitor. In extreme cases, pure, dry nitrogen under positive pressure can be used. These methods will seldom be practicable with working equipment, but they may offer the most attractive solution in transport or storage, especially since they are often very effective against the particular hazards of these conditions. Temporary protectives (Section 15.3) may also be used.

The most important corrosive agents to be considered are water vapour, acid fumes (particularly sulphur dioxide) salts and hydrogen sulphide. Water plays an essential part in stimulating attack by all the other agents, except hydrogen sulphide, so that drying the atmosphere is the most important single means of preventing corrosion. Control of other contaminants will, however, be important where satisfactory drying is not practicable.

Control of Relative Humidity

At high relative humidity the common corrosive agents produce a film of aqueous electrolyte on exposed metal surfaces. No significant corrosion results on iron, zinc, aluminium, copper or their alloys (apart from tarnishing by hydrogen sulphide), unless the relative humidity is above 60% (Section 2.2). In packaging and storage, the relative humidity is usually kept below 50%. Packages are most conveniently protected with desiccants, but for larger volumes, drying by cooled surfaces may be used, and in store-rooms, the relative humidity can be kept down by heating.

Desiccants and Desiccated Packages

Desiccating agents used in corrosion prevention must be cheap, easy to handle and non-corrosive. These requirements rule out many of the familiar laboratory desiccants, and in practice the most common packaging desiccants are silica gel, activated alumina and quicklime (calcium oxide). Activated

clays are sometimes also used, and for very low relative humidities, molecular sieves.

Silica gel and activated alumina present few practical problems. They are easily reactivated after use by heating in a ventilated oven, to 130–300°C for silica gel, and 150–700°C for activated alumina. British standard specifications have been published for desiccants for packaging^{1,2}, which regulate the contents of soluble chloride and sulphate, dust content and absorptive capacity.

Quicklime is less easy to handle, and swells considerably on hydration. It is cheap, however, and is often used on open trays to protect process equipment, machinery, furnaces, etc. during shut-down periods. If it is accidentally flooded with water, the slurry of hydrated lime provides an alkaline medium in which uncoated steel surfaces will remain without rusting.

Packages intended for use with desiccants must have low permeability to water vapour. It is therefore necessary to consider the design of the package in relation to the storage life required. This subject is beyond the scope of the present work, and guidance should be sought from standard textbooks on packaging³. The B.S.I. Packaging Code⁴ includes sections on desiccants, temporary protectives and the use of various types of packaging materials.

The following formulae are used for calculating the weight of desiccant required for a given package:

1. For tropical storage with average water-vapour pressure 3.2 kN/m²

$$W = 40ARM + \text{Dunnage Factor}$$

2. For temperate storage with average water-vapour pressure 1.0 kN/M²

$$W = 11ARM + \text{Dunnage Factor}$$

3. For completely impervious packages:

$$W = \frac{V}{6} + \text{Dunnage Factor}$$

Where W = weight (g) of 'basic desiccant' (i.e. one which absorbs 27% of its dry weight of moisture in an atmosphere maintained at 50% r.h. at 25°C),

A = area (m²) of the surface of the desiccated enclosure,

D = weight (g) of hygroscopic blocking, cushioning and other material inside the barrier (including cartons, etc.),

M = maximum time of storage (months),

R = water-vapour transmission rate of the barrier (g m⁻² d⁻¹) measured at 90% r.h. differential and 38°C and

V = volume (litre) of the air inside the barrier.

Dunnage Factor is $D/5$ for timber with moisture content higher than 14%, $D/8$ for felt, carton board and similar materials, and $D/10$ for plywood and timber with moisture content less than 14%.

Rates of transmission may be affected by creasing, scoring, etc. especially for waxed papers, and of course also strongly depend on thickness. Information can be obtained from suppliers of materials, or measurements can be made according to a method given in BS 3177:1959⁶ which includes a table

of representative values. General guidance on materials is also given in Sections 7 and 21 of the B.S.I. Packaging Code.

Air transport may set up pressure differences that disrupt the water vapour barrier of a package, expelling some of the air present at ground level and chilling the contents. Admission of warm, moist air on landing may produce heavy condensation on the contents. BS 1133, section 20, advocates the use of pressure-relief valves for packages for air freight⁴.

With desiccants with absorptive capacities differing from 27%, the weight calculated from these formulae will need to be proportionately adjusted. Packs of desiccant are obtainable commercially containing quantities stated in terms of basic desiccant.

Dry Storage and Dry Rooms

Storage rooms are similar in principle to packages, but the rate of entry of moisture is less predictable. Replacement of the air and diffusion of water vapour will have a considerable effect on the atmosphere with building materials other than glass and metals, and will vary markedly with weather conditions.

Desiccating agents can be exposed on open trays in store rooms, but in some cases, continuous circulation of the air through the desiccant may be preferable. Finely divided desiccant should be prevented from reaching exposed metal surfaces.

In most cases, however, the air is dried by condensation on a cooled surface, or the relative humidity is lessened without actually removing water vapour by heating the store (Section 2.2). Some practical points need to be considered in these cases:

1. Ventilation is necessary in heated stores, even if the heaters do not themselves produce water vapour, for otherwise the relative humidity will probably rise because water vapour is desorbed from building materials. Ventilation is even more important if gas or kerosine heaters are used.
2. The relative humidity of the air must be measured in relation to the temperature of the metal surfaces to be protected. If incoming air at 83% relative humidity at 13°C is heated to 18°C, its relative humidity will fall to 60%, but if it then comes into contact with surfaces at 10°C or below, condensation will occur until their temperatures rise sufficiently to prevent it. This situation can arise with massive metallic objects during a sudden change in the weather, or if temperature is allowed to fluctuate between day and night. It may thus be necessary to keep a store heated in summer as well as in winter, and to heat sufficiently to keep the average relative humidity as low as 30% if the maximum is not often to exceed 50%. The relative humidity and temperature of the store should be measured and recorded regularly if this method of preventing corrosion is to be operated economically and effectively.
3. Condensation may lead to corrosion when components are placed in relatively impervious wrappings in warm and humid workrooms or stores and then transferred to cold surroundings, and this should be taken into account in choosing the packaging technique.

Elimination of Contaminants

Many common materials are not severely corroded even at high relative humidity so long as the surfaces are clean, and dust particles and gaseous contaminants are eliminated from the air. It is seldom practicable to rely entirely on this method of protection, although copper and silver can be protected from tarnishing by wrappings impregnated with salts of copper, lead or zinc⁶, which react with hydrogen sulphide. Elimination of contaminants is nevertheless desirable, since it will minimise damage if other measures (such as desiccation) become ineffective during storage, and also because it will often improve the performance of the object in its ultimate application.

Surface cleaning as a preparation for coatings is discussed in Sections 11.1 and 11.2. It is important to control degreasing baths to prevent accumulation of water and formation of corrosive products which will contaminate the atmosphere as well as the objects being degreased. In the case of trichlorethylene, stabilisers are added to prevent formation of hydrochloric acid⁷. Exclusion of dust is beneficial, and may necessitate filtering the air or use of a temporary protective.

Sweat residues These contain fatty acids and sodium chloride, and increase the risk of corrosion after handling. Components should be washed in a solution of 5% water in methanol.

Packaging materials Materials to be used in contact with metals should be as free as possible from corrosive salts or acid. BS 1133, Section 7:1967 gives limits for non-corrosive papers as follows: chloride, 0.05% (as sodium chloride); sulphate, 0.25% (as sodium sulphate) and pH of water extract 5.5–8.0. Where there is doubt, contact corrosion tests may be necessary in conditions simulating those in the package.

Organic materials Corrosive vapours are sometimes emitted by organic materials used either in packaging or in the manufactured article, and may be troublesome in confined spaces. Some woods, particularly unseasoned oak and sweet chestnut, produce acetic acid (see Section 18.10), and certain polymers used in paints, adhesives and plastics may liberate such corrosive vapours as formic acid and hydrogen sulphide⁸. It may be necessary to carry out exposure trials, particularly where materials capable of liberating formaldehyde or formic acid are involved. Most corrosion problems of this kind can be prevented by using desiccants, and in many cases they are confined to imperfectly cured materials. For an excellent review see Reference 9.

Volatile Corrosion Inhibitors

Atmospheric corrosion can be prevented by using volatile inhibitors which need not be applied directly to the surfaces to be protected. Most such inhibitors are amine nitrites, benzoates, chromates, etc. They are mainly used with ferrous metals. There is still some disagreement as to the mechanism of action. Clearly, any moisture that condenses must be converted to an inhibitive solution. There is no doubt that the widely used volatile inhibitors are effective in aqueous solutions containing moderate

concentrations of chloride and sulphate, and it appears that in most cases, the effective inhibitor could equally well be applied as an ester or the sodium salt. On this view, amine salts would be useful in practice for avoiding acid conditions, or because their volatility makes them convenient (see below), rather than for any specific effect of the amine, e.g. in preventing adsorption. Certain free amines have considerable effect as volatile inhibitors. It should be said, however, that a large variety of substances, such as β -naphthol or *m*-dinitrobenzene, have some inhibitive action¹⁰ and some of these may act by hindering wetting of the metal surface. A more recent development is the use of compounds containing reducible nitro groups, which are thought to act by stimulating the cathodic process, thus assisting anodic polarisation. An inhibitor of this type, hexamethyleneimine 3:5 dinitrobenzoate, is said to be in use in the CIS, and appears to be effective with a wide range of metals¹¹.

Commercially available inhibitors differ in respect of volatility, the pH of the aqueous solution, and in attacking some metals while protecting others. The choice of inhibitor may therefore involve a compromise. In order to secure protection in rather aggressive conditions, it may be necessary to choose a relatively volatile inhibitor, which is quickly transferred into the vapour, so that condensed moisture is made innocuous as it forms. This will be particularly necessary with large structures. Such a material, however, will also be quickly lost from the enclosure compared with one less volatile and therefore slower acting. It may be advantageous to use a more alkaline inhibitor where there is contamination by acid fumes, and mixed inhibitors have been employed on this basis. It has been suggested that inhibitors could be designed to control volatility, alkalinity, etc. It is extremely difficult to devise a laboratory test for volatile corrosion inhibitors in conditions simulating those in a typical package, and convincing evidence is seldom available to show that a new formulation is superior to the commercially available materials.

Dicyclohexylammonium nitrite¹² (DCHN) has a solubility of 3.9 g in 100 g of aqueous solution at 25°C, giving a solution pH of about 6.8. Its vapour pressure at 25°C appears to be about 1.3×10^{-3} N/m², but the value for commercial materials depends markedly on purity. It may attack lead, magnesium, copper and their alloys and may discolour some dyes and plastics. Cyclohexylammonium cyclohexyl carbamate (the reaction product of cyclohexylamine and carbon dioxide, usually described as cyclohexylamine carbonate or CHC)^{13,14} is much more volatile than DCHN (vapour pressure 53 N/m² at 25°C), and much more soluble in water (55 g in 100 cm³ of solution at 25°C, giving a pH of 10.2). It may attack magnesium, copper, and their alloys, discolour plastics, and attack nitrocellulose and cork. It is said to protect cast iron better than DCHN, and to protect rather better in the presence of moderate concentrations of aggressive salts.

Both these materials are available commercially as powders and in impregnated wrapping papers and bags. Various modified inhibitors are also available, containing mixtures of the two, or more alkaline materials such as guanidine carbonate. Other proprietary inhibitors contain volatile amines, e.g. morpholine, combined with solution inhibitors. Certain solution inhibitors have been reported to act to some extent as volatile inhibitors,

e.g. sodium nitrite¹⁴. On the whole, the use of these materials appears to be consistent with the principles stated above, and they provide a very convenient means of protection, particularly for complex, not-too-large equipment, where the surfaces are not too heavily contaminated, and conditions of enclosure are reasonably good. Dosages of 35 g/m³ of free space, or 11 g/m² of surface have been recommended for packages. CHC may have some advantage in large, impervious structures, such as boilers, box girders, etc. if openings can be fitted with caps. Volatile inhibitors containing borate (for zinc) and chromate (for copper and its alloys) have been discussed in the literature, but little commercial development appears to have taken place in the UK. A review of inhibitors against atmospheric corrosion is given by Rosenfel'd and Persiantseva¹⁵.

Volatile inhibitors can be applied as loose powder in trays, by insufflation, in sachets, in tapes, in applicators containing impregnated foam, in sprays, or in impregnated wrappings. They have the obvious advantages that the packaging can be less elaborate than that required with desiccants and that equipment can be used immediately on opening the package, without the need for cleaning or stripping temporary protectives. Also, since the inhibitor may be effective at high relative humidity, or even under gross wetting, the protection may persist for a time even if the package is damaged. The application needs to be carefully considered in the light of the design and materials of construction of the equipment and its package and the cleanliness of the surfaces.

Commercial suppliers recommend precautions against breathing the vapour or dust, skin contact and ingestion in food etc., and against ignition of dust or vapour from heated surfaces.

Acknowledgement

Extracts from the British Standards Packaging Code BS 1133, Section 7:1967 and Section 19:1968 quoted in this section are reproduced by permission of the British Standards Institution, 2, Park Street, London, W1A 2BS, from whom copies of the complete standard may be obtained.

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17.2 Corrosion Inhibition: Principles and Practice

Introduction

Corrosion may be described* as 'the undesirable reaction of a metal or alloy with its environment' and it follows that control of the rate of process may be effected by modifying either of the reactants. In 'corrosion inhibition', additions of certain chemicals are made to the environment, although it should be noted that an aqueous environment can, in some cases, be made less aggressive by other methods, e.g. removal of dissolved oxygen or adjustment of pH.

Environments are either gases or liquids, and inhibition of the former is discussed in Section 17.1. In some situations it would appear that corrosion is due to the presence of a solid phase, e.g. when a metal is in contact with concrete, coal slurries, etc. but in fact the corrosive agent is the liquid phase that is always present[†]. Inhibition of liquid systems is largely concerned with water and aqueous solutions, but this is not always so since inhibitors may be added to other liquids to prevent or reduce their corrosive effects – although even in these situations corrosion is often due to the presence of small quantities of an aggressive aqueous phase, e.g. in lubricating oils and hydraulic fluids (see Section 2.11).

The majority of inhibitor applications for aqueous, or partly aqueous, systems are concerned with three main types of environment:

1. Natural waters, supply waters, industrial cooling waters, etc. in the near-neutral (say 5–9) pH range.
2. Aqueous solutions of acids as used in metal cleaning processes such as pickling for the removal of rust or rolling scale during the production and fabrication of metals, or in the post-service cleaning of metal surfaces.
3. Primary and secondary production of oil and subsequent refining and transport processes.

Following a brief discussion of inhibitor classifications and of types of chemicals used as inhibitors, the principles and practice of inhibition are

*A more precise definition of corrosion is provided by ISO in ISO 8044 (see Reference 120).

[†]Attack of metal surfaces by the mechanical action of solid materials is properly described as erosion and is not discussed here.

considered in terms of the principal factors affecting inhibitor performance (Principles) and the systems in which inhibitors are used (Practice).

Inhibitor Classifications

A number of methods of classifying inhibitors into types or groups are in use but none of these is entirely satisfactory since they are not mutually exclusive and also because there is not always general agreement on the allocation of an inhibitor to a particular group. Some of the main classifications—used particularly for inhibitors in near-neutral pH aqueous systems—are as follows.

'Safe' or 'dangerous' inhibitors Each inhibitor must be present above a certain minimum concentration for it to be effective (*see* Principles), and this classification relates to the type of corrosion that will occur when the concentration is below the minimum, or critical, value. Thus, when present at insufficient concentration a 'safe' inhibitor will allow only a uniform type of corrosion to proceed at a rate no greater than that obtaining in an uninhibited system, whereas a 'dangerous' inhibitor will lead to enhanced localised attack, e.g. pitting, and so in many cases make the situation worse than in the absence of an inhibitor.

Anodic or cathodic inhibitors This classification is based on whether the inhibitor causes increased polarisation of the anodic reaction (metal dissolution) or of the cathodic reaction, i.e. oxygen reduction (near-neutral solutions) or hydrogen discharge (acid solutions).

Oxidising or non-oxidising inhibitors These are characterised by their ability to passivate the metal. In general, non-oxidising inhibitors require the presence of dissolved oxygen in the liquid phase for the maintenance of the passive oxide film, whereas dissolved oxygen is not necessary with oxidising inhibitors.

Organic or inorganic inhibitors This distinction is based on the chemical nature of the inhibitor. However, in their inhibitive action many compounds that are organic in nature as, for example, the sodium salts of carboxylic acids, often have more similarities with inorganic inhibitors.

Other classifications Authors in the former Soviet Union have classified inhibitors as Type *A* to include film-forming types, or Type *B* which act by de-activating the medium, e.g. by removal of dissolved oxygen. Type *A* inhibitors are then further sub-divided into *A*(i) inhibitors that slow down corrosion without suppressing it completely, and *A*(ii) inhibitors that provide full and lasting protection. From the practical aspect, a useful classification is perhaps one based on the concentration of inhibitor used. It is usually the case that inhibitors are used either at low concentrations, say less than approximately 50 p.p.m., or at rather higher levels of greater than 500 p.p.m. The determining factors in the selection of the concentration used, and hence the type of inhibitor, are the economics, disposal (effluent) problems, and the facilities available for monitoring the inhibitor concentration.

Types of Chemicals Used as Corrosion Inhibitors

Before discussing the nature of chemicals that are used specifically as corrosion inhibitors, reference must be made to two methods of water treatment that are sometimes included in descriptions of inhibitive treatments. These are, respectively, de-aeration techniques and pH control. Since the presence of dissolved oxygen is necessary to sustain the corrosion process in most aqueous systems the removal of this gas by mechanical or chemical methods is an obvious method of corrosion control. The chemicals commonly used are sodium sulphite or hydrazine. There are two distinct mechanisms involved in controlling corrosion by controlling the pH. Firstly, the pH is adjusted to ensure that the metal is exposed to a solution of a pH value at which corrosion is minimal. In the case of ferrous metals corrosion tends to decrease with pH values higher than approximately 9.0. Hence, simple additions of alkali, such as caustic soda, lime, soda ash, etc. can reduce the corrosion rate of iron and steel. On the other hand such treatment will increase the corrosion rate of other metals, particularly of aluminium and its alloys, and so pH adjustment is not advisable in mixed metal systems. Secondly, the pH is adjusted to give deposition of thin protective carbonate scales from waters of suitable composition. For water saturated with calcium bicarbonate a rise in pH will cause precipitation of calcium carbonate. The pH adjustment to achieve this can be determined from the Langelier (*see* Section 2.3) or Ryzner Stability Indices; these require a knowledge of the pH of the actual system and of the pH of the water when it is saturated with calcium carbonate. It must be emphasised that such calculations measure only the scale forming propensity of the water, and are not direct measurements of the extent of corrosion reduction since other factors can influence the degree of protection afforded by the scale.

A common feature of both these methods is that the quantity of treatment chemical can be calculated from stoichiometric relationships* in the reactions involved. This is not so with conventional inhibitor treatments. With these the concentration of inhibitive chemicals can only be determined on the basis of experimental laboratory studies, service trials and overall practical experience.

The scientific and technical corrosion literature has descriptions and lists of numerous chemical compounds that exhibit inhibiting properties. Of these only a very few are ever actually used in practical systems. This is partly due to the fact that in practice the desirable properties of an inhibitor usually extend beyond those simply relating to metal protection. Thus cost, toxicity, availability, etc. are of considerable importance as well as other more technical aspects (*see* Principles). Also, as in many other fields of scientific development, there is often a considerable time lag between laboratory development and practical application. In the field of inhibition the most notable example of this gap between discovery and application is the case of sodium nitrite. Originally reported in 1899² to have inhibitive properties, it remained effectively unnoticed until the 1940s³; it is now one of the most widely employed inhibitors.

Some examples from recently published review papers will indicate the

*In practice an excess over the stoichiometric requirement, e.g. of sulphite for de-aeration, is used.

wide range of chemicals that show inhibitive properties. Hersch *et al.*⁴ in an extensive laboratory study examined over 70 compounds many of which were good inhibitors. Trabanelli *et al.*⁵ in discussing organic inhibitors list and discuss some 150 compounds. Extensive reviews by Indian workers include those on inhibitors for aluminium and its alloys⁶ (225 references) and for copper⁷ (93 references). Corrosion inhibitors in industry have been reviewed by Rama Char⁸ (134 references). More detailed studies of the properties and uses of individual inhibitors also yield much useful data as, for example, that by Walker⁹ who gives 92 references in discussing the use of benzotriazole as an inhibitor of copper corrosion. In addition to reviews of this type there are a number of books entirely devoted to the subject of corrosion inhibition, of which two have been available since the early 1960s^{1,10}.

For near-neutral aqueous solutions the function of inhibitors of the anodic class is generally considered to be that of assisting in the maintenance, repair or reinforcement of the natural oxide film that exists on all metals and alloys. Typical examples of such inhibitors for mild steel include the soluble chromates, dichromates, nitrites, phosphates, borates, benzoates and salts of other carboxylic acids. Some (nitrites and chromates) are oxidising compounds, whereas others show no oxidising capability. The 'safe' or 'dangerous' aspect of these inhibitors varies considerably and depends very much on circumstances. In the presence of aggressive ions, i.e. those that oppose the action of inhibitors (*see* The Composition of the Liquid Environment), the oxidising type tend, when present in insufficient quantity for complete protection, to give localised attack. However, the non-oxidising type, e.g. benzoate¹¹, can also show this type of behaviour but to a less marked extent. Other compounds used in near-neutral aqueous solutions include polyphosphates, silicates, zinc ions, tannins and soluble oils. These are usually assigned to the cathodic class although some are reported to affect the anodic reaction. Their function is to precipitate thin adherent films on cathodic areas of the corroding metal surface thus preventing access of oxygen to these sites. Zinc ions can react with cathodically produced hydroxyl ions to produce insoluble hydroxides that are partially protective. Similar reactions lead to the formation of films incorporating phosphates and silicates. In general these cathodic inhibitors are considered safe, i.e. not giving rise to localised attack in non-protective conditions.

The extent of inhibition afforded to metals other than mild steel depends on the metal and the inhibitor (*see* The Nature of the Metal, and Dissimilar Metals in Contact). The cathodic type of inhibitor is perhaps less susceptible than the anodic type to the nature of the metal. However, cathodic inhibitors are usually less efficient (although performing quite satisfactorily in many systems) in terms of reduction in corrosion rate, than are anodic inhibitors. The latter, when used in adequate concentrations, can often achieve 100% protection.

In a very few cases there are inhibitors that have been developed for the protection of specific metals, e.g. sodium mercaptobenzothiazole and benzotriazole for preventing the corrosion of copper.

In acid conditions oxide films are not usually present on the metal surface and the cathodic reaction is primarily that of hydrogen discharge rather than oxygen reduction. Thus, inhibitors are required that will adsorb or bond directly onto the bare metal surfaces and/or raise the overpotential for hydrogen ion discharge. Inhibitors are usually organic compounds

having N, S or O atoms with free (donor) electron pairs. There are exceptions to this bonding principle: some quaternary ammonium compounds with no donor electrons have inhibitive properties in acid solutions.

In modern practice, inhibitors are rarely used in the form of single compounds—particularly in near-neutral solutions. It is much more usual for formulations made up from two, three or more inhibitors to be employed. Three factors are responsible for this approach. Firstly, because individual inhibitors are effective with only a limited number of metals the protection of multi-metal systems requires the presence of more than one inhibitor. (Toxicity and pollution considerations frequently prevent the use of chromates as ‘universal’ inhibitors.) Secondly, because of the separate advantages possessed by inhibitors of the anodic and cathodic types it is sometimes of benefit to use a formulation composed of examples from each type. This procedure often results in improved protection above that given by either type alone and makes it possible to use lower inhibitor concentrations. The third factor relates to the use of halide ions to improve the action of organic inhibitors in acid solutions. The halides are not, strictly speaking, acting as inhibitors in this sense, and their function is to assist in the adsorption of the inhibitor on to the metal surface. The second and third of these methods are often referred to as *synergised* treatments.

Principles

The nature of the metal Since the majority of inhibitors are specific in their action towards particular metals, an inhibitor for one metal may have no effect and even an adverse effect on other metals. Table 17.1 is a general guide to the effectiveness of various inhibitors for metals in the near-neutral pH

Table 17.1 General guide to the effectiveness of various inhibitors in the near-neutral pH range

<i>Metal</i>	<i>Inhibitor</i>						
	<i>Chromates</i>	<i>Nitrites</i>	<i>Benzoates</i>	<i>Borates</i>	<i>Phosphates</i>	<i>Silicates</i>	<i>Tannins</i>
Mild steel	Effective	Effective	Effective	Effective	Effective	Reasonably effective	Reasonably effective
Cast iron	Effective	Effective	Ineffective	Variable	Effective	Reasonably effective	Reasonably effective
Zinc and zinc alloys	Effective	Ineffective	Ineffective	Effective	—	Reasonably effective	Reasonably effective
Copper and copper alloys	Effective	Partially effective	Partially effective	Effective	Effective	Reasonably effective	Reasonably effective
Aluminium and aluminium alloys	Effective	Partially effective	Partially effective	Variable	Variable	Reasonably effective	Reasonably effective
Lead-tin soldered joints	—	Aggressive	Effective	—	—	Reasonably effective	Reasonably effective

range. In addition, the compound dodecamolybdophosphate is reported¹² as approaching chromates in its ability to prevent the corrosion of a number of metals. However, there is at present only one reported application in practical systems (see Inhibitors in Practice: Central Heating Systems).

It must be emphasised that anions usually considered aggressive towards some metals can actually reduce or even prevent corrosion of other metals in certain situations, thus effectively becoming inhibitors. For example, although nitrates^{11,13,14} can prevent the inhibitive action of benzoate, chromate, nitrite, etc. towards mild steel they can be incorporated into some inhibited antifreeze formulations to reduce the corrosion of aluminium alloys. Nitrates have also been reported¹⁵ as the only inhibitors capable of preventing the stress-corrosion cracking of type 304 stainless steel. On the other hand inhibitors are necessary to prevent the corrosion of mild steel in ammonium nitrate solutions¹⁶. Sulphates generally behave as aggressive ions towards mild steel and other metals in waters, but can inhibit the chloride-induced pitting of stainless steels¹⁷ and caustic embrittlement in boilers.

Dissimilar metals in the same system Because of the specific action of many inhibitors towards particular metals, problems arise in systems containing more than one metal. In the majority of cases these problems can be overcome by the choice of a formulation incorporating inhibitors for the protection of each of the metals involved. With this procedure it is necessary not only to maintain an adequate concentration of each of the inhibitors but also to ensure that they are present in the correct proportion. This is because of two effects: firstly, failure to inhibit the corrosion of one metal may intensify the attack on the other metal; the best example of this is with aluminium and copper in the same system, and failure to inhibit copper corrosion—usually achieved with sodium mercaptobenzothiazole or benzotriazole—can lead to increased corrosion of the aluminium as a result of deposition of copper from copper ions in solution on to the aluminium surface. Secondly, an inhibitor of the corrosion of one metal may actually intensify the corrosion of another metal. Thus, benzoate is usually used to prevent the corrosion of soldered joints by nitrite inhibitor added to protect cast iron in the same system. A benzoate:nitrite ratio of greater than 7:1 is necessary in these cases.

Inhibitors can also lead to the co-called 'polarity-reversal' effects. In corrosive environments the zinc coating on galvanised steel acts sacrificially in preventing the corrosion of any exposed steel. However, in the presence of sodium benzoate^{18,19} or sodium nitrite²⁰ steel exposed at breaks in the zinc coating may corrode quite readily.

Nature of the metal surface Clean, smooth, metal surfaces usually require a lower concentration of inhibitor for protection than do rough or dirty surfaces. Relative figures for minimum concentrations of benzoate, chromate and nitrite necessary to inhibit the corrosion of mild steel with various types of surface finish have been given in a recent laboratory study^{11,13,14}. These results show that benzoate effectiveness is particularly susceptible to surface preparation. It is unwise, therefore, to apply results obtained in laboratory studies with one type of metal surface preparation to other surfaces in practical conditions. The presence of oil, grease or corrosion products on metal surfaces will also affect the concentration of inhibitor required with the

added danger of a marked depletion of inhibitor during service as a result of its chemical reaction with these contaminants. It is thus advisable to remove such contaminants before commencing inhibitor treatment. This can be done mechanically, but chemical cleaning may often be necessary. A particular method of preparing rusted surfaces is that involving the phosphate-delayed-chromate (P.D.C.) technique^{21,22}, in which the system is first treated with an acid phosphate solution to remove rust prior to the introduction of chromate inhibitor. The latter can then be used at a lower concentration than might otherwise have been necessary.

Nature of the environment This is usually water, an aqueous solution or a two- (or more) component system in which water is one component. Inhibitors are, however, sometimes required for non-aqueous liquid systems. These include pure organic liquids (Al in chlorinated hydrocarbons); various oils and greases; and liquid metals (Mg, Zr and Ti have been added to liquid Bi to prevent mild steel corrosion by the latter²³). An unusual case of inhibition is the addition of NO to N₂O₄ to prevent the stress-corrosion cracking of Ti-6Al-4V fuel tanks when the N₂O₄ is pressurised²⁴.

In at least one case water may itself act as an inhibitor, as in the corrosion of titanium by methanol²¹.

In all circumstances it is important to ensure that the inhibitor is chemically compatible with the liquid to which it is added. Chromates, for example, cannot be used in glycol antifreeze solutions since oxidation of glycol by chromate will reduce this to the trivalent state which has no inhibitive properties.

Composition of the liquid environment The ionic composition, arising from dissolved salts and gases, has a considerable influence on the performance of inhibitors. In near-neutral aqueous systems the presence of certain ions tends to oppose the action of inhibitors. Chlorides and sulphates are the most common examples of these aggressive ions, but other ions, e.g. halides, sulphides, nitrates, etc. exert similar effects. The concentration of inhibitor required for protection will depend on the concentrations of these aggressive ions. Laboratory tests^{11,13,14,26} have given some quantitative relationships between inhibitor (C_i) and aggressive ion (C_a) concentrations that will provide protection for mild steel. These are of the form

$$\log C_i = K \log C_a + \text{constant}$$

where K is related to the valencies of the respective ions.

Although halide ions are aggressive in near-neutral solutions they can be used to improve the action of inhibitors in acid corrosion (*see Practice: Acid Solutions*). Variations exist among the halides, e.g. chloride ions favour the stress-corrosion cracking of Ti in methanol whereas iodide ions have an inhibitive action²⁷.

Dissolved solid and gaseous impurities can also affect the pH of the system and this may often lead to decreased inhibitor efficiency. In industrial plant, cooling waters can take up SO₂, H₂S or ammonia and pH control of inhibited waters will be necessary. The leakage of exhaust gases into engine coolants is an example in which corrosion can occur despite the presence of inhibitors.

pH of the system All inhibitors have a pH range in which they are most effective and even in nominally 'neutral' solutions close pH control is often necessary to ensure the continued efficiency of inhibitive treatments. Nitrites lose their effectiveness below a pH of 5.5–6.0; polyphosphates should be used between pH 6.5 and 7.5; chromates, although less susceptible to pH changes, are generally used at about pH 8.5; silicates can be used over a wide pH range but the $\text{Na}_2\text{O}:\text{SiO}_2$ ratio depends on the pH value of the water.

Temperature of the system When inhibitors are used in the 0–100°C range it is usually found that higher concentrations become necessary at the higher temperatures^{11,13,14}. Other inhibitors can lose their effectiveness altogether as the temperature is raised. A prime example of this is the polyphosphate type of inhibitor. This is effective in circulating systems at temperatures below about 40°C, but at higher temperatures reversion to orthophosphate can occur and this species is ineffective at the concentrations at which it will then be present. If calcium ions are present, additional loss of inhibitor will occur due to calcium phosphate precipitation.

Inhibitor concentration To be fully effective all inhibitors require to be present above a certain minimum concentration. In many cases the corrosion that occurs with insufficient inhibitor may be more severe than in the complete absence of inhibitor (see 'Safe' and 'Dangerous' inhibitors). Not only is the initial concentration of importance but also the concentration during service. Inhibitor depletion may occur for a variety of reasons. In the initial stages of use, i.e. after the first application, the inhibitor concentration may fall off rapidly due to its reaction with contaminants in the system and also as a result of protective film formation. Thus, initial concentrations of inhibitor are often recommended to be at higher levels than those subsequently to be maintained. Losses may also occur due to mechanical rather than chemical effects as, for example, with windage losses in cooling towers, blow-down in boilers, and leakages generally.

Maintenance of a correct inhibitor concentration (level) is particularly important where low-level treatments, e.g. less than 100 p.p.m. are used. Such treatments are, however, usually applied (for economic and effluent reasons) in large capacity systems, and plants of this nature will usually have skilled personnel available for control purposes. In smaller closed systems, e.g. automobile engines, higher concentrations of more than approximately 0.1% are commonly used, but in these applications there is usually a good reserve of inhibitor allowed for in the recommended concentration and routine checking is of less importance. Nevertheless, since these inhibitors are often of the 'dangerous' type, gross depletion may lead to enhanced corrosion.

Inhibitor control can be effected by conventional methods of chemical analysis, inspection of test specimens or by instrumentation. The application of instrumental methods is becoming of increasing importance particularly for large systems. The techniques are based on the linear (resistance) polarisation method and the use of electrical resistance probes. They have the advantage that readings from widely separated areas of the plant can be brought together at a central control point. (See Section 18.1.)

Mechanical effects Corrosion can often be initiated or intensified by the conjoint action of mechanical factors. Typical examples include the presence of inherent or applied stresses, fatigue, fretting or cavitation effects. Inhibitors that are effective in the absence of some or all of these phenomena may not be so in their presence. In fact it may not always be possible to use inhibitors successfully in these situations and other methods of corrosion prevention will be required.

Aeration and movement of the liquid For the majority of inhibitors in near-neutral aqueous systems an adequate supply of dissolved oxygen is necessary for them to function properly. The dissolved oxygen present in solutions that are in equilibrium with atmospheric air is adequate for this purpose, but in systems that have become de-aerated the non-oxidising type of inhibitor may not be fully effective. Even in aerated systems the transport of oxygen and inhibitor to the metal surface is assisted by the movement of the solution. In fact, quiescent solutions may require higher concentrations of inhibitor than do circulation systems. Butler²⁸ has shown, for example, that polyphosphates (normally applied only to flowing solutions) can inhibit under quiescent conditions but at much higher concentrations. However, there are reported instances of excessive aeration having an adverse effect on inhibitor performance*. The action of tannins is partly associated with their effects at the metal surface, i.e. as conventional inhibitors, and partly with their ability to react with and remove dissolved oxygen. In heavily aerated systems these inhibitors may be less effective due to depletion by this latter effect.

Presence of crevices, dead-ends, etc. Effective protection by inhibitors relies on the continued access of inhibitor to all parts of the metal surface (see Aeration and Movement of the Liquid). It frequently happens that this condition is difficult to achieve due to the presence of crevices at joints, dead-ends in pipes, gas pockets, deposits of corrosion products, etc. Corrosion will then occur at these sites even though the rest of the system remains adequately protected.

Effects of micro-organisms There are three main effects that can arise as a result of the presence of micro-organisms in aqueous solutions: (a) direct bacterial participation in metal corrosion usually due to the action of sulphate-reducing bacteria in anaerobic conditions or of the *Thiobacillus* and *Ferrobacillus* genera in aerobic conditions; the action of these organisms can lead to the accumulation of large amounts of corrosion product and pitting of the metal; (b) accumulation of flocculent fungal growths that can impede water flow and (c) breakdown and hence depletion of inhibitors by bacterial attack.

Many inhibitors will lose their effectiveness in the presence of one or more of these effects. Indeed inhibitors may act as nutrient sources for some microbial organisms. In these circumstances it will be necessary to incorporate suitable bactericides in the inhibitor formulations.

*Apart from extreme cases involving cavitation effects.

Scale formation Controlled scale deposition by the Langelier approach or by the proper use of polyphosphates or silicates is a useful method of corrosion control, but uncontrolled scale deposition is a disadvantage as it will screen the metal surfaces from contact with the inhibitor, lead to loss of inhibitor by its incorporation into the scale and also reduce heat transfer in cooling systems. Apart from scale formation arising from constituents naturally present in waters, scaling can also occur by reaction of inhibitors with these constituents. Notable examples are the deposition of excess amounts of phosphates and silicates by reaction with calcium ions. The problem can be largely overcome by suitable pH control and also by the additional use of scale-controlling chemicals.

Toxicity, disposal and effluent problems With the increasing awareness of environmental pollution problems, the use of and disposal of all types of treated waters is receiving greater attention than ever before. This often places severe restrictions on the choice of inhibitor, particularly where disposal of large volumes of treated water is involved. The disposal of chromate and phosphate inhibitor formulations is important in this respect and there is an increasing move towards the low-chromate-phosphate types of formulation. In fact for some applications even this approach is not acceptable and inhibitor formulations containing bio-degradable chemicals are being introduced.

Other considerations In addition to the above general factors affecting inhibitor application and performance, there will be other special effects relating to particular types of systems, e.g. in oil-production technology. Some of these are referred to in appropriate cases in the following section.

Inhibitors in Practice

A difficulty arises in describing the precise chemical nature of many inhibitor formulations that are actually used in practice. With the advancing technology of inhibitor applications there are an increasing number of formulations that are marketed under trade names. The compositions of these are, for various reasons, frequently not disclosed. A similar problem arises in describing the composition of many inhibitor formulations used in the former Soviet Union. Here the practice is to use an abbreviated classification system and it is often difficult to trace the actual composition, although in many cases a judicious literature search will provide the required information.

The following discussion is thus restricted to inhibitor formulations that can be described in chemical terms.

Aqueous Solutions and Steam

Potable Waters

In these waters there is a severe limitation on inhibitor choice because of the potability and toxicity factors. As pointed out by Hatch²⁹, the possibilities

are limited to calcium carbonate scale deposition, silicates, polyphosphates and zinc salts. Silicates do not prevent corrosion completely and their inhibitive effect is more marked in soft waters. The molar ratio $\text{Na}_2\text{O}:\text{SiO}_2$ is important. For example, Stericker³⁰ has proposed $\text{Na}_2\text{O}:3\cdot3\text{SiO}_2$ at 8 p.p.m. for most waters, but $\text{Na}_2\text{O}:2\cdot1\text{SiO}_2$ is preferred if the pH is below 6·0. Concentrations of 4–10 p.p.m. are recommended, and the method of application is often by by-passing part of the flow through a silicate (water-glass) reservoir, the slow dissolution giving the required inhibitor concentration in the main flow. With polyphosphates the most efficient inhibition is obtained in the presence of divalent ions such as Ca^{2+} or Zn^{2+} ; in fact the Ca^{2+} :polyphosphate ratio is more important than the actual concentration. A minimum value of 1:5 has been given for this ratio with an overall concentration of up to 10 p.p.m. The optimum pH is in the 5–7 range and the inhibitive action is often improved by the addition of zinc salts. Hatch²⁹ points out that the treatment concentration depends on the nature of the water distribution system. Thus, with small towns a feed of 5 p.p.m. is needed to provide a residual of 0·5–1 p.p.m. whereas for the more compact systems in cities a feed of 1 p.p.m. is often sufficient. The action of the inhibitor is affected by existing deposits in the mains, and higher initial doses of about 10 p.p.m. are often required. Even higher dosages, say 50–100 p.p.m., can be used for cleaning old mains.

Cooling Systems

For the purposes of corrosion inhibition these may be broadly divided into three types: (a) 'Once-through', in which the cooling water runs continually to waste as in the condenser systems using seawater; (b) 'open', in which cooling towers are used to dissipate heat taken up by the cooling water elsewhere; (c) 'closed' in which the cooling water is retained in the system, the heat being given up via a heat-exchanger as in refrigeration plant, vehicle cooling systems, etc. Systems (a) and (b) are generally much larger in terms of water-capacity and metal area than those of type (c).

Once-through systems Where mild steel is the primary metal of construction, this usually being so for low-chloride waters, simple treatments with lime and soda can be effective in making the water less aggressive. Of the conventional inhibitors, polyphosphates at 2–10 p.p.m. with small amounts of zinc ions will reduce tuberculation but not necessarily the overall corrosion rate³¹. The use of 9 p.p.m. of an organo-activated zinc-phosphate-chromate inhibitor has been described³² and this can be replaced, although with some loss in effectiveness, by 10 p.p.m. of polyphosphate if effluent problems exist. Effluent and economic problems in fact limit the choice of inhibitors, and the solution to the corrosion problem may lie in selecting a more suitable material of construction. Mild steel is often avoided and non-ferrous alloys such as the cupro-nickels and aluminium brasses are employed. These alloys are normally resistant even in aerated saline waters but corrosion problems can arise. Small amounts of iron, arising from the alloy or from elsewhere in the system, contribute towards the resistance of these alloys. Bostwick³³ showed the advantage of adding FeSO_4 to seawater condenser systems, and recently Brooks³⁴ confirmed that 1 p.p.m. of this chemical added three times daily

for about 1 h to power-house intakes has contributed 25–30% to the life of the condenser tubes. More recently high-molecular-weight water-soluble polymers of, for example, the non-ionic polyacrylamide type have been described³⁵ for inhibiting the corrosion of cupro-nickel condenser tubes.

Open recirculating systems These are more amenable to inhibition since it is possible to maintain a closer control on water composition. Corrosion inhibition in these systems is closely allied to a number of other problems that have to be considered in the application of water treatment. Most of these arise from the use of cooling towers, ponds, etc. in which the water is subject to constant evaporation and contamination leading to accumulation of dirt, insoluble matter, aggressive ions and bacterial growths, and to variations in pH. A successful water treatment must therefore take all these factors into account and inhibition will often be accompanied by scale prevention and bactericidal treatments.

The controlled deposition of thin adherent films of calcium carbonate is probably the cheapest method of reducing corrosion, but may not always be entirely satisfactory because local variations in pH and temperature will affect the nature and extent of film deposition.

Treatment with conventional inhibitors is very much governed by environmental constraints. In the mid-twentieth century the choice was probably restricted to chromate or nitrite. For chromates Darrin³⁶ emphasised the need for a high initial dosage of 1 000 p.p.m. subsequently lowered to 300–500 p.p.m. The principal drawbacks of this method are the possibility of localised attack if chloride or sulphate contents rise during operation and the environmental problems. Sodium nitrite used at about 500 p.p.m. is also susceptible to chloride and sulphate and the pH control (7.0–9.0) is probably more important than with chromates. Nitrite is susceptible to bacterial decomposition and can give rise, particularly if reduced to ammonia, to stress-corrosion cracking of copper-base alloys. However, nitrite is used with success in cooling tower systems. Bacterial decomposition of nitrite can be controlled with bactericides. In air-cooling systems Conoby and Swain³⁷ quote the use of a shock treatment of 2,2'-methylene bis (4-chloro-phenol) at 100 p.p.m. and a weekly addition of sodium penta-chlor phenate to control algae formation.

On the low-level treatment side, polyphosphates, variously described as glassy phosphates, hexametaphosphate, etc. have been used as corrosion inhibitors. The concentrations recommended are somewhat above those used in 'threshold treatment' to control scale deposition. The most effective protection is obtained in the presence of an adequate quantity of calcium, magnesium or zinc ions. In general a polyphosphate: calcium ratio expressed as $P_2O_5:Ca$ of not greater than 3.35:1 is recommended. The overall concentration will vary with conditions, but for cooling towers this falls in the 15–37 p.p.m. (as P_2O_5) range. When starting treatment, a higher initial dosage is required, this may be as high as 100 p.p.m. Fisher³² suggests an initial dosage of 20 p.p.m. for a corroded steel cooling system dropping to 10 p.p.m. after one week's operation. The application and properties of poly-phosphates have been reviewed by Butler³⁸ and by Butler and Ison³⁹. Polyphosphate inhibitors are subject to some limitations that are mainly concerned with reversion to orthophosphate and subsequent scale deposition

if the calcium concentration is high. Some difficulties with their use have been summarised by Beecher *et al.*⁴⁰.

Silicates at about 20–40 p.p.m. are also used in cooling-water treatment although the build-up of protection can be slow. At higher temperatures calcium silicate may be deposited from hard waters.

Modern practice, on grounds of economy and avoidance of pollution, is towards the use of a combination of inhibitors at low concentration levels. Four main types of compound are involved, *viz.* chromates, polyphosphates, zinc salts and organic materials, and these are used in various combinations^{31,41}. The principle involved is to combine a cathodic with an anodic type of inhibitor, e.g. zinc ions and/or polyphosphate with chromate. These mixed inhibitor systems usually require an operating pH of 6–7⁽⁴²⁾ and thus should only be used where pH control facilities are available. Typical formulations include 10–12 p.p.m. of a 1:4 $\text{Na}_2\text{Cr}_2\text{O}_7$:Zn mixture⁴³ which provides good inhibition of copper as well as of steel corrosion, and 35 p.p.m. of a zinc-chromate-organic mixture. The latter introduces 12 p.p.m. of CrO_4^{2-} and 3–5 p.p.m. of Zn^{2+} (added as ZnSO_4) into the water, the organic compound is described as a powerful surface-active agent⁴⁰. The zinc-dichromate method is further improved by adding phosphate and sometimes organic compounds such as lignosulphonates and synthetic polymers. Comeaux⁴¹ has listed the constituents of nine commercially available inhibitors. Each of these contains chromate and zinc with the CrO_4 :Zn ratio varying from 0.92 to 30.0, five contain phosphate with Zn: PO_4 from 0.1 to 3.24 and three contain organic compounds. In some formulations of the zinc-phosphate type the organic compound will be of the mercaptobenzothiazole type to inhibit corrosion of copper³¹. Five to ten p.p.m. of poly-phosphate is said³¹ to assist the inhibitive action of 20–40 p.p.m. of silicate but it is still important to avoid calcium silicate deposition on heat transfer surfaces. However, in recommending a silicate-complex phosphate inhibitor (25 p.p.m. at pH 6.5–8.0) Ulmer and Wood⁴⁴ state that scale formation is not a problem if the silicate is below 100 p.p.m., except if film boiling occurs, when scaling would occur in any case. The use of 100 p.p.m. of orthophosphate plus 40 p.p.m. of chromate plus 10 p.p.m. of polyphosphate has also been recommended⁴⁵.

As anti-pollution requirements become more demanding the use of even these low-level chromate-phosphate treatments is not always approved. New inhibitor formulations employ more acceptable bio-degradable organic compounds, often in conjunction with zinc ions. A formulation consisting of an organic heterocyclic compound plus zinc salt plus an 'alkalinity stabilising agent' has been described⁴⁶ applied initially at 500 and then at 100 p.p.m. Organic phosphorus-containing compounds have been introduced for scale control but also for corrosion inhibition. These are salts of aminomethylenephosphonic acid (AMP)^{31,47}. In conjunction with zinc salts they can be used in place of other treatments and have the advantage that close pH control is not required. Corrosion inhibitors compounded from zinc salts and derivatives of methanol phosphonic acid are described in a US patent⁴⁸. Although AMP was one of the first phosphonic acids to be introduced for scale and corrosion inhibition there are now a number of related compounds available and in wide use. These include 1-hydroxyethylidene 1, 1'-diphosphonic acid (HEDP), nitrilo-tris-phosphonic acid (NTP), phosphono-butane-tetra carboxylic acid (PBTC), etc.

Closed recirculating systems This type of system is most commonly encountered in the cooling of internal combustion engines. Inhibitors are required for engine coolants in order to prevent corrosion of the constructional metals, to prevent blockage of coolant passages by corrosion products and to maintain heat-transfer efficiency by keeping metal surfaces free from adherent corrosion products. The problem is often associated with inhibition of antifreeze solutions which are almost invariably ethanediol*-water solutions. When uninhibited these can become acid due to oxidation of the ethanediol in operating conditions. However, inhibition is also important with water coolants that are used in the summer months⁴⁹. The best practice is to use inhibited antifreeze throughout the year changing it annually.

Road vehicles Numerous formulations exist for coolant inhibition in road vehicles. The inhibitors most frequently encountered are nitrite, benzoate, borax, phosphate, and the specific copper inhibitors sodium mercaptobenzothiazole (NaMBT) and benzotriazole. Various combinations of these are in use. In the UK three compositional British Standards namely BS 3150, 3151 and 3152 were in use for many years. However, advances in other formulations and a general move towards performance rather than compositional specifications have resulted in the withdrawal of BS 3150-2. Nevertheless, a brief description of these formulations is given, as they illustrate various aspects of inhibitor properties and use. BS 3150 contains triethanolammonium orthophosphate (T.E.P.), which is prepared by neutralising 0.9-1.0% H_3PO_4 with triethanolamine so that the pH of a 50% aqueous solution is 6.9-7.3, and NaMBT (0.2-0.3%). This formulation was based on the original work of Squires⁵⁰. The T.E.P. protects ferrous metals and aluminium alloys and the NaMBT protects copper and copper alloys. In the absence of NaMBT corrosion of copper can occur leading to marked attack on aluminium alloys. The NaMBT concentration becomes depleted with time, but experience indicates that with normal usage in road vehicles an annual replacement of the whole coolant will give satisfactory results. BS 3151 contained 5.0-7.5% sodium benzoate plus 0.45-0.55% sodium nitrite in the undiluted ethanediol and is based on the original work of Vernon *et al.*⁵¹. The nitrite is for protection of cast iron with the benzoate to protect other metals, but more importantly to protect soldered joints against the adverse action of nitrite. The nitrite concentration depletes in service, but again a one year period of satisfactory inhibition is provided. BS 3152 contained borax (2.4-3.0% $Na_2B_4O_7 \cdot 10H_2O$). Some controversy exists as to the efficiency of borax used alone, particularly with aluminium alloys. Nevertheless, borax has been much used and service experience has shown satisfactory inhibition. More recent formulations include other inhibitors, e.g. 3% borax plus 0.1% mercaptobenzothiazole plus 0.1% sodium metasilicate ($Na_2SiO_3 \cdot 5H_2O$) plus 0.03% lime (CaO)—the percentages being % by weight of the ethanediol which is then used at 33 vol. % dilution⁵².

In the UK, a standard for describing minimum requirements for inhibited engine coolants is provided by BS 6580⁵³. (Test methods are described in BS 5117.)

Alkali-metal phosphates have been incorporated in antifreeze solutions but there are indications of unfavourable behaviour with aluminium alloys

*Ethylene glycol.

under heat-transfer conditions. Soluble oils have also been used as inhibitors but they can cause deterioration of rubber hose connections.

Locomotive diesels As larger volumes of coolant are required in railway locomotives than in road vehicles, the cost of inhibition is proportionally greater. An additional factor is the possibility of cavitation attack of cylinder liners. These considerations place a restriction on the choice of inhibitors. In the past, chromates have been used at concentrations of up to 0.4%, but their use presents handling and disposal problems. Chromates cannot be used with ethanediol antifreeze solutions. A 15:1 borate-metasilicate at a concentration of 1% has been used in the UK. Nitrate is added to this to improve inhibition of aluminium alloy corrosion. Tannins and soluble oils are also used, but probably to a lesser extent than in the past. The benzoate-nitrite formulation (formerly BS 3151) is effective and has been used by continental railways⁵⁴.

Marine diesels Again a wide number of formulations are in use. The inhibitors commonly employed include nitrites, borates and phosphates. Typical formulations include a 1:1 nitrite:borax mixture at 1250–2000 p.p.m. and pH 8.5–9.0; and 1250–2 000 p.p.m. of nitrite with addition of tri-sodium phosphate to give phenolphthalein alkalinity.

The factors affecting railway diesels apply also to marine diesels but with the additional restriction that the inhibitors must not present a toxicity hazard when the cooling system is associated with equipment for producing drinking water. This is because of the possibility of accidental leakage between the two systems.

Central Heating Systems

The principal components in these systems are a cast iron or steel boiler, copper or steel pipework, pressed steel or cast-iron radiators and a copper hot-water tank or calorifier to supply heat to domestic water. If systems are properly designed, installed and maintained, the concentration of dissolved oxygen in the circulating water—which should be subject to little make-up—is low and corrosion is minimal. Nevertheless, corrosion problems occasionally arise in these systems. Often these are associated with ingress of oxygen but this is not always so. The main problems are the perforation of pressed-steel radiators and the necessity for the frequent release of hydrogen gas from radiators. The latter effect is associated with the production of excess amounts of magnetite (Fe_3O_4) as a result of the Schikorr reaction:



Thin adherent films of magnetite form on the steel surfaces in the initial stages of operation of the system, but in troublesome situations the magnetite becomes non-adherent and in extreme cases can lead to pump blockages.

These difficulties can often be overcome with inhibitive treatments although the procedure is not acceptable where there is any possibility of inadvertent mixing of the heating water with domestic water.

The excess magnetite problem has been associated with the catalytic action of copper ions on the Schikorr reaction^{55,56}. Hence, inhibitors that will

prevent copper dissolution should reduce magnetite formation. For this purpose 0.01% benzotriazole can be added to the water. For general corrosion inhibition a mixture of 1.0%, sodium benzoate with 0.1% sodium nitrite has been successfully used in a number of installations⁵⁷⁻⁵⁹. Sodium metasilicate has been used with success, but usually in softened waters. Other workers suggest that it is not reliable due to the possibility of localised attack (results with $\text{Na}_2\text{Si}_2\text{O}_5$)⁵⁸ and because of possible pipe and pump blockage by gel-formation or precipitation of hardness salts. The use of a silicate-tannic acid treatment has also been described. A further development is the introduction, based on test rig results, of a four-component formulation containing sodium benzoate, sodium nitrite, sodium dodecylmolybdophosphate and benzotriazole⁶⁰.

Some corrosion inhibitors can encourage the production of fungal growths in the relatively static cold water in the header tanks of these systems. Biocides will then often need to be included in the inhibitor formulation.

Steam-condensate Lines

The causes and inhibition of corrosion in steam-condensate lines have been reviewed by Obrecht⁶¹. The major causes of corrosion are carbon dioxide and oxygen and the problems are associated not only with damage to the pipes, which may be of steel but often of copper-base alloys, but also with iron and copper pick-up which will be deposited elsewhere in the circuit. Neutralisation treatments can be employed to keep the pH in the 8.5-8.8 region⁶². Typical compounds used for this purpose are ammonia, cyclohexylamine, morpholine and benzylamine. An important requirement is that these agents should condense at the same rate as the steam. This is not necessarily so with ammonia and pockets of unneutralised condensate may occur. Furthermore, ammonia can cause attack of copper-base alloys. The amines, except at high concentrations, are less aggressive in this respect, they have better distribution characteristics and condense at the same rate as the steam. An important disadvantage with these materials is their cost, since about 3 p.p.m. are needed per p.p.m. of carbon dioxide⁶² and so they tend to be used only in high recovery systems.

Inhibitive (as opposed to purely neutralisation) techniques now employ long-chain aliphatic amines with alkyl groups containing 8-22 carbon atoms⁶¹⁻⁶³. The most effective are the straight-chain aliphatic primary amines with C_{10-18} , the best known example being octadecylamine and its acetate salt. They are used at a total concentration of only 1-3 p.p.m. and are effective against carbon-dioxide and oxygen-induced corrosion. They function by producing a non-wettable film on the metal surfaces. The acetate salt is used to facilitate dispersion and solubilisation. The most effective distribution is achieved by injection into the boiler or the main steam header. The protective film ceases to form at about 200°C⁶³ and in a condensing turbine system inhibition will be provided through the feed system up to the point where the feed reaches this temperature. These inhibitors have been successfully applied to prevent exfoliation of 70 Cu-30 Ni tubes⁶¹.

Contrary to the method of application of inhibitors to water systems, the

initial addition of filming amine should be at a lower concentration than that subsequently used. This is because the surface-active nature of the amine will loosen and remove existing corrosion products and these will accumulate elsewhere in the system. A cleaning-up phase of up to a month may therefore be necessary to avoid these effects.

High-chloride Systems

(sea-water, desalination, refrigerating brines, road de-icing salts, etc.)

Complete inhibition of corrosion in waters containing high concentrations of chloride is difficult, if not impossible to achieve economically. Despite this, many such systems make use of inhibitors to give marked reductions in corrosion rates.

In refrigerating brines, chromates at a pH of about 8–8.5 have been widely used. Concentrations recommended are between 2 000 and 3 300 p.p.m. corresponding to the 125 and 200 lb (56.7 and 90.7 kg) of sodium dichromate per 1 000 ft³ (28.32 m³) for calcium or sodium chloride brines, respectively, recommended by the American Society of Refrigerating Engineers.

In diluted sea-water high concentrations of sodium nitrite can bring about a reduction in the corrosion of steel. For example, corrosion in 50% sea-water can be inhibited with 10% sodium nitrite⁶⁴, and 3–7% of this inhibitor has been recommended for preventing the corrosion of turbine journals due to sea-water ingress⁶⁵. The beneficial effects of mixtures of chromates and phosphates have been reported⁶⁶. Combinations of these inhibitors have been examined with respect to preventing corrosion in desalination plant. Oakes *et al.*⁶⁷ have reported good results with 5 p.p.m. of chromate plus 30–45 p.p.m. of Na₂HPO₄. Legault *et al.*⁶⁸ conclude that three mixtures are effective for mild steel in oxygen-saturated sea-water at 121°C, i.e. dichromate plus phosphate at 50 p.p.m., chromate plus phosphate plus zinc plus iodide at 100 p.p.m. and chromate plus phosphate at 50 p.p.m. The chromate:phosphate ratio is usually 1:1 with Na₃PO₄ as the phosphate.

Various opinions exist as to the value of inhibitors⁶⁹ in road de-icing salts. Chromates have been advocated but to a limited extent because of the toxicity effects. In general, the most widely used inhibitors are the polyphosphates, either alone or in conjunction with other inhibitors. The use of polyphosphates on roads in Scandinavia has been reported⁷⁰, although difficulties arise with loss of inhibitor by absorption in the sand that is mixed with the salt. Extensive laboratory tests conducted in the UK showed⁷¹ that polyphosphates were more effective in preventing further rusting of damaged painted panels than in preventing the corrosion of bare steel. A further development is to compound the polyphosphate with an organic-type inhibitor^{72,73}.

Acid Solutions

Probably the major use of inhibitors in acid solutions is in pickling processes. The chief requirements of the inhibitor are that it should not decompose during the life of the pickle, not increase hydrogen absorption by the metal

and not lead to the formation of surface films with electrically insulating properties that might interfere with subsequent electroplating or other surface treatments.

A wide variety of compounds are used in acid inhibition. These are now mainly organic compounds usually containing N, S or O atoms, although inorganic arsenic and antimony compounds have been used in the past. In general, for the pickling of steel, as pointed out for example by Machu⁷⁴, sulphur-containing compounds are preferred for sulphuric acid solutions and nitrogen-containing compounds for hydrochloric acid solutions. Every and Riggs⁷⁵ list 76 individual compounds and 32 mixtures that were subjected to laboratory tests and concluded that often a mixture of N— and S— compounds was better than either type alone. The superiority of S— compounds for inhibition in sulphuric acid is borne out in the list of 112 compounds quoted by Uhlig⁷⁶. Twelve of the fourteen most effective compounds listed contain S atoms in the molecule. Typical of these are phenylthiourea, di-ortho-tolyl-thiourea, mercaptans and sulphides, 90% protection being provided with 0.003–0.01% concentrations.

N— compounds used as acid inhibitors include heterocyclic bases, such as pyridine, quinoline and various amines. Carassiti⁷⁷ describes the inhibitive action of decylamine and quinoline, as well as phenylthiourea and dibenzylsulphoxides for the protection of stainless steels in hydrochloric acid pickling. Hudson *et al.*^{78,79} refer to coal tar base fractions for inhibition in sulphuric and hydrochloric acid solutions. Good results are reported with 0.25 vol. % of distilled quinoline bases with addition of 0.05M sodium chloride in 4N sulphuric acid at 93°C. The sodium chloride is acting synergistically, e.g. 0.05M NaCl raises the percentage inhibition given by 0.1% quinoline in 2N H₂SO₄ from 43 to 79%. Similarly, potassium iodide improves the action of phenylthiourea⁸⁰.

Acetylenic compounds have been described for inhibition in acid solutions^{81–83}. Typical inhibitors include 2-butyne-1,4-diol, 1-hexyne-3-ol and 4-ethyl-1-octyne-3-ol.

An exception to the 'lone pair' or 'donor' electron requirement of organic inhibitors is provided by the quaternary ammonium compounds. Meakins^{84,85} reports the effectiveness of tetra-alkyl ammonium bromides with the alkyl group having C ≥ 10. Comparative laboratory tests of commercial inhibitors of this type have been described⁸⁶. The inhibiting action of tetra-butyl ammonium sulphate for iron in H₂S-saturated sulphuric acid has been described, better results being achieved than with mono-, di- or tri-butylamines⁸⁷.

In the former Soviet Union much use is made of industrial by-products to prepare acid inhibitors. The PB class is obtained by treating technical butyraldehyde with ammonia and polymerising the resulting aldehyde-ammonia. PB-5, for example, with 0.01–0.15% of an arsenic salt is used in 20–25% HCl. A mixture of urotropine (hexamethyleneimine, hexamine) with potassium iodide, a regulator and a foaming agent is the ChM inhibitor. BA-6 is prepared from the condensation product of hexamine with aniline. A more recent development is the Katapin series which consists of *p*-alkyl benzyl pyridine chlorides; Katapin A, for example, is the *p*-dodecyl compound.

The beneficial effect of chloride ions on inhibitor action is brought out in

the acid descaling of ships' tanks while at sea⁸⁸. Inhibited 0.75% sulphuric acid prepared with sea-water can be used for this process at ambient temperatures, the chloride present in the sea-water acting synergistically with the inhibitor.

In the practice of acid pickling a foaming agent is often added to the pickling bath in order to facilitate penetration of the rust and scale by the inhibited acid and also to provide a foam blanket to prevent spray coming from the bath. After removal from the bath the metal is rinsed well, finally in hot water and then often dipped in a mild alkali, phosphate or chromate bath, to provide short term protection before the next operation. A suggested variation on this procedure is to follow the acid pickling by a hot water rinse in a bath with a 35 mm layer of stearic acid on the bath surface. As the metal is withdrawn through this a water repellent film is left on its surface.

The Oil Industry

Corrosion problems requiring the application of inhibitors exist in the oil industry at every stage of production from initial extraction to refining and storage prior to use. Comprehensive reviews of these inhibitors have been given by Bregman^{10,90}. Four main processes are involved. (a) Primary production, (b) secondary production, (c) refining and (d) storage, and each of these may be further subdivided.

Primary production Although the technology of the process has many variations, the common factor is that oil flows from the deposit through steel tubing to the surface. Corrosion problems arise due to the presence of water that invariably accompanies the oil. It has been shown⁹¹ that corrosivity is related to the water content which can vary over a wide range. This water can contain a variety of corrosive agents including carbon dioxide, hydrogen sulphide, organic acids, chlorides, sulphates, etc. Wells containing H₂S are referred to as *sour* and those free from H₂S as *sweet*; the former are the more corrosive. In some sweet wells the crude oil itself can provide protection of the metal if the oil: water ratio is suitable, but this effect will not be found in sour wells.

Most of the inhibitors in use are organic nitrogen compounds and these have been classified by Bregman⁹⁰ as (a) aliphatic fatty acid derivatives, (b) imidazolines, (c) quaternaries, (d) rosin derivatives (complex amine mixtures based on abietic acid); all of these will tend to have long-chain hydrocarbons, e.g. C₁₈H₃₇ as part of the structure, (e) petroleum sulphonic acid salts of long-chain diamines (preferred to the diamines), (f) other salts of diamines and (g) fatty amides of aliphatic diamines. Actual compounds in use in classes (a) to (d) include: oleic and naphthenic acid salts of *n*-tallowpropylenediamine; diamines RNH(CH₂)_xNH₂ in which R is a carbon chain of 8–22 atoms and *x* = 2–10; and reaction products of diamines with acids from the partial oxidation of liquid hydrocarbons. Attention has also been drawn to polyethoxylated compounds in which the water solubility can be controlled by the amount of ethylene oxide added to the molecule.

The method of inhibitor *application* varies considerably since so many factors have to be considered. These include the oil: water ratio, the types

of oil and the water composition, the fluid velocity, temperature, type of geological formation, emulsion formation, economics, method of well completion, solubility and specific gravity of the inhibitor, etc. It has been stated⁹² that there are over 20 methods of introducing an inhibitor into the well to ensure that it enters the producing stream. These include: 'slug' treatment in which regular injections of inhibitors are made with automatic injection equipment; 'batch' treatments in which sufficient inhibitor is added to last for a month or longer; 'weighted' treatments⁹³ in which organic weighting agents can raise the density of the inhibitor formulation thus assisting its dispersal; 'micro-encapsulation'⁹⁴ methods with a liquid inhibitor weighted and coated with a water-soluble sheath to give controlled release at a given temperature; 'squeeze'^{95,96} technique where the inhibitor is displaced under pressure into the geological formation whence it is absorbed into the rock and then gradually desorbed into the deposit. All these and other methods are subject to their particular advantages and disadvantages which are discussed in the relevant technical literature.

Secondary recovery In this, water is forced down into the strata to displace further quantities of oil. This water can be that initially obtained from the well or it can be taken from other convenient sources. In either case the probability is that the water will be of an aggressive nature. As the water is now being forced down into the deposit there is the danger of blockage of the geological formation by corrosion products and this is an added reason for inhibition. Apart from the presence of dissolved salts there are the major problems of the oxygen and bacterial contents. Sulphite additions may be made to deal with dissolved oxygen but the method is not so straightforward⁹⁷ as, for example, in boiler-water treatment. Thus, care is required in brines containing H_2S as the catalyst* may be precipitated as sulphide. The sulphite may be lost in the deposition of calcium sulphite hemihydrate if the calcium concentration is high.

As in primary production, organic nitrogen compounds are often used since many of these have dispersant properties that will prevent the formation of adherent deposits⁹⁰. It has been suggested that dissolved oxygen can prevent long-chain amines from being fully effective as corrosion inhibitors. Nevertheless some inhibitors of this type appear to be immune to this effect, for example see the results of Jones and Barrett⁹⁸. Oxygen removal has been combined with long-chain amine treatment by using a 40% methanol solution of the oleyldiamine adduct of SO_2 —the so-called ODASA method⁹⁹. A concentration of 25 p.p.m. of this inhibitor is quoted for the scavenging of 1 p.p.m. of oxygen and field trials have shown reductions in oxygen from 0.5 to less than 0.1 p.p.m. Inorganic inhibitors can also be used in waterflood treatment to limit oxygen corrosion; a zinc-glassy phosphate type at 12–15 p.p.m. and pH 7.0–7.2 has been described¹⁰⁰. Silicates at 100 p.p.m. have also been used.

A particular problem in oil recovery arises in the acidising process for stimulating well production in limestone formations^{74,101,102}. For many years 15% hydrochloric acid for this process has been successfully inhibited with commercially available organic inhibitors to minimise attack on the

*Small amounts (less than 1 p.p.m.) of cobalt salts are usually added to the sulphite to catalyse its reaction with oxygen.

steel equipment. Sodium arsenite with a surfactant has been used⁷⁴, although problems can occur subsequently at the refining stage due to catalyst poisoning. In a discussion of acetylenic-type inhibitors Tedeschi *et al.*¹⁰³ show that the action of compounds such as hexynol and ethyl octynol for this type of application can be improved by the use of nitrogen synergists such as ethylene diamine, dimethyl formamide, urea or ammonia. However, with the advent of deeper wells this concentration of acid is not so effective and 28–30% concentrations become necessary. These higher concentrations, and the higher temperatures at the well-bottom, together place a limitation on the existing inhibitors. Research is active in this field, e.g. in one case a survey of some 20 000 compounds was made from which it was concluded that acetylenic compounds and some nitrogen compounds offered promise¹⁰¹. Russian workers¹⁰⁴ have described the inhibitor ANP-2 for use with 20% HCl in acidising. This is the HCl salt of aliphatic amines with an amine number of 15·75 obtained from the nitration of paraffins. At 0·1–0·15%, ANP-2 reduced the corrosion of steel at 43°C in 20% HCl by 20 times.

Refining Inhibitors are necessary in the processing of crude oil — particularly where steel is involved — since many of the process fluid constituents are corrosive. Copper-bearing alloys, e.g. admiralty metal, are also used and the problem of controlling steel corrosion is often made more difficult by the need to use methods that will not enhance the corrosion of non-ferrous parts of the system. In general the corrosive agent is the water in the oil stream and its corrosivity is increased by the presence of H₂S, CO₂, O₂, HCl and other acids (naphthenics can be a source of corrosion). As in so many other situations the problem of inhibition cannot be considered in isolation. Problems concerned with fouling and scaling must be taken into account and comprehensive reviews of these problems have been published^{90, 105}. Since many of the corrosion problems are due to the presence of acids one remedy is to adjust the pH to 7·0–7·5 by adding sodium hydroxide, sodium carbonate or ammonia. At higher pH values ammonia can lead to corrosion, and possibly stress-corrosion cracking of copper-base alloys. The neutralisation of hydrochloric acid with ammonia will produce ammonium chloride and deposits of solid NH₄Cl can be corrosive even in the absence of water¹⁰⁶. Other disadvantages of alkali treatment are those of expense and the necessity for pH control to prevent scale formation.

Nitrogen-containing organic inhibitors, often in conjunction with ammonia, are now widely used. These compounds are usually of similar types to those for primary production, because, as Bregman has pointed out, the corrosive agents are often the same in the two cases. This author has reviewed the compounds used and points out that most are imidazoline derivatives. He cites Brooke¹⁰⁷ for specific applications. Thus, 6 p.p.m. of an imidazoline with ammonia to pH 7·5 added to the overhead of a crude topping unit increased the length of a run from 6 to 18 months. In another application, corrosion of overhead condensers and the top tray of a distillation column was prevented by the use of 4 p.p.m. of an amino alkyl aryl phosphate soluble in light hydrocarbons. This had to be changed to 4 p.p.m. of a methylene oxide rosin amine type of inhibitor after the phosphate was found to cause deposits when the produced fuel was used in internal

combustion engines. This last observation is a further example of factors other than those relating only to the metal-environment reaction influencing the selection of an inhibitor. The possible adverse effect of inhibitors on process catalysts in refineries must also be considered.

Storage Corrosion is again mainly associated with the presence of water which separates at the bottom of storage tanks. Inhibition in this water layer can be achieved with the highly soluble inorganic inhibitors. Nitrites, silicates, polyphosphates, etc. have been used as well as oil-soluble inhibitors. Organic inhibitors include imidazolines alone or with other inhibitors, itaconic salts, oleic acid salts of various amines and polyalkene glycol esters of oleic acid. Again there are other requirements that must be fulfilled apart from prevention of corrosion.

Reinforced Concrete

Inhibitors to prevent or retard the corrosion of steel reinforcing bars in concrete have been discussed on a number of occasions. Treadaway and Russell¹⁰⁸ consider the important considerations to be (a) the extent of inhibition, (b) the rate of inhibitor consumption, (c) the type of attack if inhibition fails and (d) the effect of the inhibitor on concrete strength. Of these (d) is of considerable importance^{108, 109}. The best practice appears to be the coating of the bars with a strong inhibitive slurry rather than a general incorporation into the concrete mix as a whole. The inhibitors generally considered applicable are sodium benzoate¹¹⁰ (2–10% in a slurry coating); sodium nitrite^{111, 112} and sodium benzoate plus sodium nitrite¹⁰⁸. A mixture of grease with Portland cement, sodium nitrite, casein and water applied as a ≥ 1 mm layer coating for reinforcing bars has been described¹¹³. Sodium mercaptobenzothiazole, stannous chloride and various unidentified proprietary compounds have also been described for inhibition in concrete. Laboratory tests have been reported by Gouda *et al.*¹¹⁴.

Miscellaneous

In nitrogenous fertiliser solutions of the $\text{NH}_4\text{NO}_3\text{--NH}_3\text{--H}_2\text{O}$ type corrosion of steel can be prevented by 500 p.p.m. of sulphur-containing inhibitors, e.g. mercaptobenzothiazole, thiourea and ammonium thio-cyanate. However, these inhibitors are not so effective where most of the NH_3 is replaced by urea. For these solutions phosphate inhibitors such as $(\text{NH}_4)_2\text{HPO}_4$ and polyphosphates were more effective¹¹⁵.

In the hydraulic transport of solids through steel pipelines, inhibitors of the sodium–zinc–phosphate glass type have been shown¹¹⁶ to be effective. In the case of coal slurries the polyphosphate type was rejected because the de-oxygenating action of the coal lowered the inhibitor effectiveness. Hexavalent chromium compounds at 20 p.p.m. were more effective¹¹⁷.

In gas reforming plants, e.g. the hot potassium carbonate process for CO_2 removal, sodium metavanadate is used to prevent mild-steel corrosion¹¹⁸. Banks reports¹¹⁹ that this treatment does not reduce the rather high corrosion rate of Cu–30Ni in these plants.

Recent Developments

Terminology The International Standards Organization has recently¹²⁰ defined a corrosion inhibitor as a 'chemical substance which decreases the corrosion rate when present in the corrosion system at a suitable concentration, without significantly changing the concentration of any other corrosive agent.' This last point is significant since it excludes chemicals employed for deaeration or pH control from the definition of a corrosion inhibitor. On the other hand, it should be noted that the inhibitor is '... present in the corrosion system ...', and thus arsenic when added to brasses to prevent dezincification may be classified as an inhibitor.

Literature Recent additions to the literature on the principles and practice of inhibition include books concerned with the subject as a whole, and reports of conferences and papers, or reports concentrating on particular aspects of the subject. Books include the volume by the late Professor I. L. Rozenfel'd¹²¹ and collected data in the form of references, patents etc. from various sources¹²²⁻¹²⁵. Conferences include the recent quinquennial events at the University of Ferrara^{126, 127}, each providing substantial contributions to all aspects of corrosion inhibition. The uses of molybdates as inhibitors have been reviewed by Vukasovich and Farr in a paper with 221 references¹²⁸ and test methods for inhibitors in a report from the European Federation of Corrosion with 49 references¹²⁹.

General considerations The principles and practice of corrosion inhibition in recent years have become increasingly dominated by health and safety considerations. These relate to all aspects of inhibitor practice, i.e. to handling, storage, use and disposal. The problem becomes particularly important when there is the possibility of contact of inhibited media with the environment. Thus, it can be argued that the 'safety' requirements for inhibitors for solar heating systems should be more rigid than those for engine cooling systems since in the former case small leaks in heat exchangers could lead to contamination of domestic water.

Open Recirculating Systems

The matter of environmental protection has been recognised for some years in the inhibition of open recirculating systems, although the technical advances that have been made in this period in inhibitor formulation have also been prompted by other requirements, for example, the need to avoid scale deposits. Since the 1940s there has been a move away from the use of chromates at relatively high concentrations to formulations with lower concentrations and eventually to non-chromate treatments. This situation has come about as a result of a better understanding of the role of other types of chemicals in the inhibition process, notably phosphorus-containing compounds, organics (e.g. triazoles), zinc salts and polymeric compounds.

The sequence of formulation types may be deduced from p. 17:21 and may be summarised as: high levels of chromate; low levels, of chromate, but with polyphosphates; further reductions in chromate by the introduction of zinc ions; and polyphosphate instability overcome by the use of phosphates and

metal-free, i.e. no chromium or zinc, formulations achieved by the use of polymeric chemicals. Organic inhibitors of the triazole or mercaptobenzothiazole classes are added when protection of copper is a particular requirement. The polymeric compounds were introduced to assist in controlling scale deposition and generally for keeping systems free from deposits and suspended matter. These materials are long-chain polymers containing repeating carboxyl groups with molecular weights of several thousands. Examples include polyacrylates, polymaleics and various copolymers. The mechanism of their action in contributing to corrosion inhibition is not fully understood but must be associated in some way with the maintenance of clean surfaces.

Although chemicals in closed circulation systems do not generally come into contact with the environment – except perhaps on disposal – problems can exist with safety in handling. A particular example is the need for caution in the mixing of coolants containing nitrites with those containing amines because of the possible production of carcinogenic nitrosoamines. This caution has been expressed in other fields of use of inhibitors (see below).

Solar Heating Systems

The requirements for inhibitors in solar heating systems are in some ways similar to those for domestic central heating systems but in other respects to those for engine cooling systems. A significant difference from the latter is the need, in many parts of the world, for the presence of an anti-freeze agent. Since ethanediol is toxic, the more acceptable propanediol (propylene glycol) tends to be used together with relatively non-toxic corrosion inhibitors such as silicates, phosphates, BTA, etc. A particular requirement is the need for high-temperature stability since surface temperatures of panels exposed to sunlight can be well in excess of 100°C. Polymeric compounds have also been put forward as inhibitors for solar heating systems as described, for example, in a patent application in 1982 for a polymerisable acid graft copolymer, e.g. acrylic acid-(oxyethylene-oxypropylene) copolymer together with a silicate¹³¹.

Refrigerating Brines

For many years such media have been based on strong salt solutions, e.g. calcium chloride brines. Sodium dichromate has been used (see p. 17:26), but recently other inhibitors have been claimed to be effective. One patent quotes *N*-alkyl-substituted alkanolamines, e.g. 2-ethyl ethanolamine + BTA at pH 9.0¹³¹. A mixture of hydrazine hydrochloride + BTA¹³² has been claimed as well as a mixture of gelatin + triethanolamine + potassium dihydrogen phosphate¹³³. Other examples are to be found in the patent literature and the above are quoted to illustrate the diversity of chemicals that may be used.

Absorption-type refrigerators operating with strong lithium bromide solutions can also be inhibited by a number of chemicals. Thus, a mixture of lithium hydroxide + BTA + sodium molybdate has been reported¹³⁴.

Elsewhere, in a series of Japanese patents, mixtures of resorcinol + sodium nitrate, glycerine + sodium nitrate, lithium hydroxide + tungstate, etc., have been claimed to be effective. An example of the use of inhibited cooling mixtures of low toxicity is provided by a patent¹³⁵ which describes a mixture of silicate + polyphosphate + a saccharide, e.g. sucrose or fructose, as the inhibitor formulation in a propylene glycol + potassium-hydrogen-carbonate mixture used in aluminium cooler boxes for ice-cream.

Metal Working Coolants

There has been much activity in this field of corrosion inhibition in recent years which appears to have been prompted by health and safety requirements. As with engine coolants, the use of nitrites, particularly where amines may also be present, needs to be considered carefully. Nitrites have been widely used in cutting, grinding, penetrating, drawing and hydraulic oils. Suggested replacements for nitrites and/or amines make use, *inter alia*, of various borate compounds, e.g. monoalkanolamide borates. Molybdates have also been proposed in conjunction with other inhibitors, e.g. carboxylates, phosphates, etc.¹³⁶. Water-based metalworking fluids usually contain other additives in addition to corrosion inhibitors, e.g. for hard-water stability, anti-foam, bactericidal properties and so on. Thus, claims are made for oil-in-water emulsions with bactericidal and anti-corrosion properties.

Oil and Gas Production, Transport and Storage

This is a prolific field for inhibitors although the main types remain as grouped by Bergmann (see p. 17). In this application of inhibitors, probably more than in any other, the methods of introducing the inhibitor into the corrosive environment receive as much attention as the nature of the inhibitor. The most severe conditions are those met in acidising treatments, typically with 15–35% hydrochloric acid at high downhole temperatures.

Compounds with triple bonds, i.e. acetylenic compounds, continue to receive attention. Patents have been filed for mixtures of propargyl alcohol with, for example, cellosolve + a phenol formaldehyde resin + tar bases¹³⁷ heterocyclic nitrogen compounds + acetylenic + dialkylthiourea¹³⁸ or a quaternary + antimony oxide¹³⁹.

With the increasing development of sour, i.e. H₂S-containing wells there is a need to assess the performance of inhibitors in such contaminated environments. Reports of inhibitor performance often make special reference to performance in the presence of H₂S, which can be accompanied by CO₂. Schmitt has emphasised the need for assessing the effects of corrosion inhibitors on the hydrogen uptake by the metal as well as the retardation of metal dissolution¹²⁶. For example, in discussing inhibitors of the quaternary ammonium type, he and his co-workers point out that, depending on the inhibitor, the H₂S present could increase or decrease the efficiency of the inhibitor in blocking, hydrogen absorption. For 10% formic acid good results have been reported with *p*-dodecylbenzylquinolinium chloride and benzylquinolinium iodide¹⁴⁰.

Gasoline

Corrosion inhibitors in gasoline are present to provide protection to the fuel distribution system which operates at ambient temperature. It is particularly important that the inhibitors do not adversely affect other requirements of the fluid, for example, in carburettor detergency. The most effective inhibitors appear to be salts, or esters, of carboxylic or phosphoric acids, often associated with long-chain radicals. Test methods for inhibition of water contaminated gasoline include NACE TM-01-72 and ASTM D6651 (IP-135). Gasohol is formed by mixing 96–95 volumes of gasoline with 5–10 volumes of ethanol. Although substantially anhydrous, the presence of small quantities of water, say up to 0.3%, can lead to corrosion. Various triazoles have been proposed¹⁴¹, e.g. 3-amino-1H-1,2,4-triazole with polyisobutylene and maleic acid anhydride. Other formulations are based on reaction products of carboxylic acids with amines. Problems associated with alcohol-gasoline corrosion have been described¹⁴².

Checklist of Steps to Minimise Corrosion by the Use of Inhibitors

1. The practice of corrosion inhibition requires that the inhibitive species should have easy access to the metal surface. Surfaces should therefore be clean and not contaminated by oil, grease, corrosion products, water hardness scales, etc. Furthermore, care should be taken to avoid the presence of deposited solid particles, e.g. stones, swarf, building materials, etc. This ideal state of affairs is often difficult to achieve but there are many cases where less than adequate consideration has been given to the preparation of systems to receive inhibitive treatment. Acid treatments, notably with 3–5% citric acid, with or without associated detergent washes, are often recommended and adopted for cleaning systems prior to inhibition. However, it is not always appreciated that these treatments will not remove particulate material particularly when, as is often the case, the material is insoluble in acids.
2. Even with adequate cleaning procedures it is still necessary to ensure that the inhibitor reaches all parts of the metal surfaces. Care should be taken, particularly when first filling, a system, that all dead ends, pockets, crevice regions, etc., are contacted by the inhibited fluid. This will be encouraged in many systems by movement of the fluid in service but in nominally static systems it will be desirable to establish a flow regime at intervals to provide renewed supply of inhibitor.
3. Inhibitors must be chosen after taking into account the nature and combinations of metals present, the nature of the corrosive environment and the operating conditions in terms of flow, temperature, heat transfer, (see 'Principles' p. 17:14).
4. Inhibitor concentrations should be checked on a regular basis and losses restored either by appropriate additions of inhibitor, or by complete replacement of the whole fluid—as recommended, for example, with engine coolants.

5. Where possible, some form of continuous monitoring should be employed, although it must be remembered that the results from monitoring devices, probes, coupons etc., refer to the behaviour of that particular component at that particular part of the system. Nevertheless, despite this caution, it must be recognised that the monitoring of the corrosion condition of an inhibited system is a well-established procedure and widely used (10:26-10:32).

Conclusions

The principles and practice of corrosion inhibition have been described in terms of the factors affecting inhibitor performance and selection (principles) and the more important practical situations in which inhibitors are used (practice). For the latter a brief account is given of the nature of the system, the reasons for inhibitor application and the types of inhibitor in use.

Tabulated results have been avoided since these are either obtained from carefully controlled laboratory tests or from specific systems and would thus require much qualification before their application to other systems.

The very wide use of inhibitors is obvious, but emphasis must always be placed on the factors affecting their performance and on the specific circumstances and other requirements relating to particular applications.

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17.3 The Mechanism of Corrosion Prevention by Inhibitors

The mechanisms of corrosion inhibition will be described separately for acid and neutral solutions, since there are considerable differences in mechanisms between these two media. Definitions and classifications of inhibitors are given in Section 17.2 and by Fischer¹.

Inhibitors for Acid Solutions

The corrosion of metals in aqueous acid solutions can be inhibited by a very wide range of substance^{2,3}. These include relatively simple substances, such as chloride, bromide or iodide ions and carbon monoxide, and many organic compounds, particularly those containing elements of Groups V and VI of the Periodic Table, such as nitrogen, phosphorus, arsenic, oxygen, sulphur and selenium. Organic compounds containing multiple bonds, especially triple bonds, are effective inhibitors. Organic compounds of high molecular weight, e.g. proteins and polysaccharides, also have inhibitive properties. The primary step in the action of inhibitors in acid solutions is generally agreed to be adsorption on to the metal surface, which is usually oxide-free in acid solutions. The adsorbed inhibitor then acts to retard the cathodic and/or anodic electrochemical processes of the corrosion. The factors influencing the adsorption and the electrochemical reactions will be considered in turn. (See also Section 20.1.)

Adsorption of Corrosion Inhibitors onto Metals

Measurements of the adsorption of inhibitors on corroding metals are best carried out using the direct methods of radio-tracer detection⁴⁻⁷ and solution depletion measurements⁸⁻¹⁰. These methods provide unambiguous information on uptake, whereas the corrosion reactions may interfere with the indirect methods of adsorption determination, such as double layer capacity measurements¹¹, coulometry¹¹, ellipsometry¹² and reflectivity¹². Nevertheless, double layer capacity measurements have been widely used for the determination of inhibitor adsorption on corroding metals, with apparently consistent results, though the interpretation¹³ may not be straightforward in some cases.

Direct measurements on metals such as iron, nickel and stainless steel have shown that adsorption occurs from acid solutions of inhibitors such as iodide ions¹⁴, carbon monoxide¹⁵ and organic compounds such as amines^{8, 10, 16}, thioureas^{9, 16-18}, sulphoxides¹⁹⁻²¹, sulphides^{21, 22} and mercaptans¹⁶. These studies have shown that the efficiency of inhibition (expressed as the relative reduction in corrosion rate) can be qualitatively related to the amount of adsorbed inhibitor on the metal surface. However, no detailed quantitative correlation has yet been achieved between these parameters. There is some evidence^{16, 23} that adsorption of inhibitor species at low surface coverage θ (for complete surface coverage $\theta = 1$) may be more effective in producing inhibition than adsorption at high surface coverage. In particular, the adsorption of polyvinyl pyridine on iron in hydrochloric acid at $\theta < 0.1$ monolayer has been found to produce an 80% reduction in corrosion rate¹⁰.

In general, the results of direct adsorption measurements provide a basis for the widely used procedure of inferring the adsorption behaviour of inhibitors from corrosion rate measurements. This involves the assumption that the corrosion reactions are prevented from occurring over the area (or active sites) of the metal surface covered by adsorbed inhibitor species, whereas these corrosion reactions occur normally on the inhibitor-free area. The inhibitive efficiency is then directly proportional to the fraction of the surface covered with adsorbed inhibitor. This assumption has been applied to deduce the effects of concentration on the adsorption of inhibitors, and to compare the adsorption of different inhibitors (usually related in structure) at the same concentration. On the whole, the interpretation in this way of the efficiency of inhibitors in terms of their adsorption behaviour has given consistent results, which have clarified the factors influencing inhibition and adsorption. However, some qualifications are necessary in this approach, since this simple relationship between inhibitive efficiency and adsorption will not always apply. As mentioned above, at low surface coverage ($\theta < 0.1$), the effectiveness of adsorbed inhibitor species in retarding the corrosion reactions may be greater than at high surface coverage^{10, 16, 23}. In other cases, adsorption of inhibitors, e.g. thioureas^{24, 25} and amines^{26, 27} from solutions of low concentration may cause stimulation of corrosion. Furthermore, in comparing the inhibitive efficiency and adsorption of different inhibitors, possible differences in the mechanism and effectiveness of retardation of the corrosion reactions must be considered²⁸.

The information on inhibitor adsorption, derived from direct measurements and from inhibitive efficiency measurements, considered in conjunction with general knowledge of adsorption from solution²⁹⁻³¹, indicates that inhibitor adsorption on metals is influenced by the following main factors.

Surface charge on the metal Adsorption may be due to electrostatic attractive forces between ionic charges or dipoles on the adsorbed species and the electric charge on the metal at the metal/solution interface. In solution, the charge on a metal can be expressed by its potential with respect to the zero-charge potential (see Section 20.1). This potential relative to the zero-charge potential, often referred to as the ϕ -potential³², is more important with respect to adsorption than the potential on the hydrogen scale, and indeed the signs of these two potentials may be different. As the ϕ -potential

becomes more positive, the adsorption of anions is favoured and as the ϕ -potential becomes more negative, the adsorption of cations is favoured. The ϕ -potential also controls the electrostatic interaction of the metal with dipoles in adsorbed neutral molecules, and hence the orientation of the dipoles and the adsorbed molecules. For different metals at the same ϕ -potential, electrostatic interactions should be independent of the nature of the metal, and this has been used as a basis to compare adsorption of inhibitors on different metals³²⁻³⁴. Thus Antropov³² has shown that the adsorption of some inhibitors on mercury can be related to their adsorption and inhibitive effect on iron, when considered at the same ϕ -potentials for both metals. The differences in behaviour of an inhibitor on various metals can also in some cases be related to the differences in ϕ -potentials at the respective corroding potentials.

The functional group and structure of the inhibitor Besides electrostatic interactions, inhibitors can bond to metal surfaces by electron transfer to the metal to form a coordinate type of link. This process is favoured by the presence in the metal of vacant electron orbitals of low energy, such as occur in the transition metals. Electron transfer from the adsorbed species is favoured by the presence of relatively loosely bound electrons, such as may be found in anions, and neutral organic molecules containing lone pair electrons or π -electron systems associated with multiple, especially triple, bonds or aromatic rings. In organic compounds, suitable lone pair electrons for co-ordinate bonding occur in functional groups containing elements of Groups V and VI of the Periodic Table. The tendency to stronger co-ordinate bond formation (and hence stronger adsorption) by these elements increases with decreasing electronegativity in the order $O < N < S < Se$ ³⁵⁻³⁷, and depends also on the nature of the functional groups containing these elements. The structure of the rest of the molecule can affect coordinate bond formation by its influence on the electron density at the functional group³⁸⁻⁴². The effects of substituents in related inhibitor molecules, e.g. pyridines^{38, 39, 43, 48}, anilines^{39, 42-45}, aliphatic amines⁴², amino acids⁴⁶, benzoic acids⁴⁷ and aliphatic sulphides⁴⁹, on the inhibitive efficiencies have been correlated with changes in electron densities at functional groups, as derived from nuclear magnetic resonance measurements³⁹, values of Hammett constants (aromatic molecules)⁴⁰⁻⁴⁷ or Taft constants (aliphatic molecules)^{42, 46, 49}, or from quantum mechanical calculations^{38, 42, 48}. The results of these investigations generally indicate that the electron density at the functional group increases as the inhibitive efficiency increases in a series of related compounds. This is consistent with increasing strength of coordinate bonding due to easier electron transfer, and hence greater adsorption. An analogous correlation has been demonstrated by Hackerman^{50, 51} between inhibitive efficiencies in a series of cyclic imines $(CH_2)_nNH$ and changes in hybrid bonding orbitals of the electrons on the nitrogen atom making electron transfer and coordinate bond formation easier.

Interaction of the inhibitor with water molecules Due to the electrostatic and co-ordinate bond interactions described under the previous two headings, the surfaces of metals in aqueous solutions are covered with adsorbed water molecules. Adsorption of inhibitor molecules is a displacement

reaction involving removal of adsorbed water molecules from the surface. During adsorption of a molecule, the change in interaction energy with water molecules in passing from the dissolved to the adsorbed state forms an important part of the free energy change on adsorption. This has been shown to increase with the energy of solvation of the adsorbing species, which in turn increases with increasing size of the hydrocarbon portion of an organic molecule³⁶. Thus increasing size leads to decreasing solubility and increasing adsorbability. This is consistent with the increasing inhibitive efficiency observed at constant concentrations with increasing molecular size in a series of related compounds^{36, 52, 53}.

Interaction of adsorbed inhibitor species Lateral interactions between adsorbed inhibitor species may become significant as the surface coverage, and hence the proximity, of the adsorbed species increases. These lateral interactions may be either attractive or repulsive. Attractive interactions occur between molecules containing large hydrocarbon components, e.g. *n*-alkyl chains. As the chain length increases, the increasing van der Waals attractive force between adjacent molecules leads to stronger adsorption at high coverage. Repulsive interactions occur between ions or molecules containing dipoles and lead to weaker adsorption at high coverage. The effects of lateral interactions between adsorbed inhibitors on inhibitive efficiency have been discussed by Hoar and Khera²⁶.

In the case of ions, the repulsive interaction can be altered to an attractive interaction if an ion of opposite charge is simultaneously adsorbed. In a solution containing inhibitive anions and cations the adsorption of both ions may be enhanced and the inhibitive efficiency greatly increased compared to solutions of the individual ions. Thus, synergistic inhibitive effects occur in such mixtures of anionic and cationic inhibitors^{54, 55}. These synergistic effects are particularly well defined in solutions containing halide ions, I^- , Br^- , Cl^- , with other inhibitors such as quaternary ammonium cations⁵⁶, alkyl benzene pyridinium cations⁵⁷, and various types of amines^{55, 58-61}. It seems likely that co-ordinate-bond interactions also play some part in these synergistic effects, particularly in the interaction of the halide ions with the metal surfaces and with some amines⁵⁵.

Reaction of adsorbed inhibitors In some cases, the adsorbed corrosion inhibitor may react, usually by electro-chemical reduction, to form a product which may also be inhibitive. Inhibition due to the added substance has been termed *primary* inhibition and that due to the reaction product *secondary* inhibition⁶²⁻⁶⁵. In such cases, the inhibitive efficiency may increase or decrease with time according to whether the secondary inhibition is more or less effective than the primary inhibition. Some examples of inhibitors which react to give secondary inhibition are the following. Sulphoxides can be reduced to sulphides, which are more efficient inhibitors^{19, 20, 21, 63, 64}. Quaternary phosphonium and arsonium compounds can be reduced to the corresponding phosphine or arsine compounds, with little change in inhibitive efficiency^{63, 64}. Acetylene compounds can undergo reduction followed by polymerisation to form a multimolecular protective film^{66, 67}. Thioureas can be reduced to produce HS^- ions, which may act as stimulators of corrosion^{24, 25, 54}.

Effects of Inhibitors on Corrosion Processes

In acid solutions the anodic process of corrosion is the passage of metal ions from the oxide-free metal surface into the solution, and the principal cathodic process is the discharge of hydrogen ions to produce hydrogen gas. In air-saturated acid solutions, cathodic reduction of dissolved oxygen also occurs, but for iron the rate does not become significant compared to the rate of hydrogen ion discharge until the pH exceeds about 3. An inhibitor may decrease the rate of the anodic process, the cathodic process or both processes. The change in the corrosion potential on addition of the inhibitor is often a useful indication of which process is retarded^{24,67}. Displacement of the corrosion potential in the positive direction indicates mainly retardation of the anodic process (anodic control), whereas displacement in the negative direction indicates mainly retardation of the cathodic process (cathodic control). Little change in the corrosion potential suggests that both anodic and cathodic processes are retarded (see Section 1.4 for appropriate potential versus current diagrams).

The effects of adsorbed inhibitors on the individual electrode reactions of corrosion may be determined from the effects on the anodic and cathodic polarisation curves of the corroding metal^{24,28,68,69}. A displacement of the polarisation curve without a change in the Tafel slope in the presence of the inhibitor indicates that the adsorbed inhibitor acts by blocking active sites so that reaction cannot occur, rather than by affecting the mechanism of the reaction. An increase in the Tafel slope of the polarisation curve due to the inhibitor indicates that the inhibitor acts by affecting the mechanism of the reaction. However, the determination of the Tafel slope will often require the metal to be polarised under conditions of current density and potential which are far removed from those of normal corrosion. This may result in differences in the adsorption and mechanistic effects of inhibitors at polarised metals compared to naturally corroding metals^{24,56,70}. Thus the interpretation of the effects of inhibitors at the corrosion potential from applied current-potential polarisation curves, as usually measured, may not be conclusive. This difficulty can be overcome in part by the use of rapid polarisation methods^{56,71}. A better procedure²⁴ is the determination of 'true' polarisation curves near the corrosion potential by simultaneous measurements of applied current, corrosion rate (equivalent to the true anodic current) and potential. However, this method is rather laborious and has been little used.

Electrochemical studies have shown that inhibitors in acid solutions may affect the corrosion reactions of metals in the following main ways.

Formation of a diffusion barrier The absorbed inhibitor may form a surface film which acts as a physical barrier to restrict the diffusion of ions or molecules to or from the metal surface and so retard the corrosion reactions. This effect occurs particularly when the inhibitor species are large molecules, e.g. proteins, such as gelatine, agar agar; polysaccharides, such as dextrin; or compounds containing long hydrocarbon chains. Surface films of these types of inhibitors give rise to resistance polarisation and also concentration polarisation affecting both anodic and cathodic reactions⁷². Similar effects also occur when the inhibitor can undergo reaction to form a multimolecular

surface film, e.g. acetylenic compounds⁶⁷ and sulphoxides^{19,73}.

Blocking of reaction sites The interaction of adsorbed inhibitors with surface metal atoms may prevent these metal atoms from participating in either the anodic or cathodic reactions of corrosion. This simple blocking effect decreases the number of surface metal atoms at which these reactions can occur, and hence the rates of these reactions, in proportion to the extent of adsorption. The mechanisms of the reactions are not affected and the Tafel slopes of the polarisation curves remain unchanged. Behaviour of this type has been observed for iron in sulphuric acid solutions containing 2,6-dimethyl quinoline²⁴, β -naphthoquinoline⁶⁹, or aliphatic sulphides⁴⁹.

It should be noted that the anodic and cathodic processes may be inhibited to different extents^{24,26,74}. The anodic dissolution process of metal ions is considered to occur at steps or emergent dislocations in the metal surface, where metal atoms are less firmly held to their neighbours than in the plane surface. These favoured sites occupy a relatively small proportion of the metal surface. The cathodic process of hydrogen evolution is thought to occur on the plane crystal faces which form most of the metal surface area. Adsorption of inhibitors at low surface coverage tends to occur preferentially at anodic sites, causing retardation of the anodic reaction. At higher surface coverage, adsorption occurs on both anodic and cathodic sites, and both reactions are inhibited.

Participation in the electrode reactions The electrode reactions of corrosion involve the formation of adsorbed intermediate species with surface metal atoms, e.g. adsorbed hydrogen atoms in the hydrogen evolution reaction; adsorbed (FeOH) in the anodic dissolution of iron^{75,76}. The presence of adsorbed inhibitors will interfere with the formation of these adsorbed intermediates, but the electrode processes may then proceed by alternative paths through intermediates containing the inhibitor. In these processes the inhibitor species act in a catalytic manner and remain unchanged. Such participation by the inhibitor is generally characterised by a change in the Tafel slope observed for the process. Studies of the anodic dissolution of iron in the presence of some inhibitors, e.g. halide ions^{14,77-79}, aniline and its derivatives^{28,43}, the benzoate ion⁷⁰ and the furoate ion⁸⁰, have indicated that the adsorbed inhibitor I participates in the reaction, probably in the form of a complex of the type $(Fe \cdot I)_{ads}$ or $(Fe \cdot OH \cdot I)_{ads}$. The dissolution reaction proceeds less readily via the adsorbed inhibitor complexes than via $(Fe \cdot OH)_{ads}$, and so anodic dissolution is inhibited and an increase in Tafel slope is observed for the reaction.

Adsorbed species may also accelerate the rate of anodic dissolution of metals, as indicated by a decrease in Tafel slope for the reaction. Thus the presence of hydrogen sulphide in acid solutions stimulates the corrosion of iron, and decreases the Tafel slope^{25,54,56}. The reaction path through $(Fe \cdot HS^-)_{ads}$ has been postulated to lead to easier anodic dissolution than that through $(Fe \cdot OH)_{ads}$. This effect of hydrogen sulphide is thought to be responsible for the acceleration of corrosion of iron observed with some inhibitive sulphur compounds, e.g. thioureas^{25,54,81}, at low concentrations, since hydrogen sulphide has been identified as a reduction product. However, the effects of hydrogen sulphide are complex, since in the presence of inhibitors such as amines⁵⁶, quaternary ammonium cations⁵⁶, thioureas^{54,81},

synergistic enhancement of inhibition is observed due to interaction of adsorbed HS^- ions with the adsorbed inhibitor.

Inhibitors may also retard the rate of hydrogen evolution on metals by affecting the mechanism of the reaction, as indicated by increases in the Tafel slopes of cathodic polarisation curves. This effect has been observed on iron in the presence of inhibitors such as phenyl-thiourea^{58,69}, acetylenic hydrocarbons^{82,83}, aniline derivatives⁸⁴, benzaldehyde derivatives⁸⁵ and pyrilium salts⁸⁵. According to Antropov⁸⁶ and Grigoryev^{84,85}, the rate determining step (which depends on experimental conditions⁷⁵) for the hydrogen evolution reaction on iron in acid solutions (pH less than 2) is the recombination of adsorbed hydrogen atoms to form hydrogen molecules. Grigoryev^{84,85} has shown that addition of anilines, benzaldehydes and pyrilium salts to hydrochloric acid tends to retard the discharge of hydrogen ions to form adsorbed hydrogen atoms on iron, so that this step rather than the recombination step tends to control the rate of the overall hydrogen evolution reaction.

Some inhibitors, e.g. amines^{26,27,33} and sulphoxides⁸⁷, which can add on hydrogen ions in acid solutions to form protonated species, may accelerate the rate of the cathodic hydrogen evolution reaction on metals, due to participation of the protonated species in the reaction. This occurs when the discharge of the protonated species to produce an adsorbed hydrogen atom at the metal surface occurs more easily than the discharge of the hydrogen ion. This effect becomes more significant as the hydrogen overvoltage of the metal increases, and so may be observed to a greater extent on zinc than on iron³³.

Alteration of the electrical double layer The adsorption of ions or species which can form ions, e.g. by protonation, on metal surfaces will change the electrical double layer at the metal-solution interface, and this in turn will affect the rates of the electrochemical reactions^{33,54}. The adsorption of cations, e.g. quaternary ammonium ions⁵⁴ and protonated amines³³ makes the potential more positive in the plane of the closest approach to the metal of ions from the solution. This positive potential displacement retards the discharge of the positively charged hydrogen ion. For the inhibition of iron corrosion by pyridines in acid solutions, Antropov³³ has calculated the theoretical inhibition coefficients of the hydrogen ion discharge reaction, due to the effect of adsorbed pyridine cations on the electrical double layer. The calculated values agreed well with observed values at low inhibitor concentrations, indicating that inhibition could be wholly attributed to electrostatic effects, and that blocking of the surface by adsorbed inhibitor is not important.

Conversely, the adsorption of anions makes the potential more negative on the metal side of the electrical double layer and this will tend to accelerate the rate of discharge of hydrogen ions. This effect has been observed for the sulphosalicylate ion⁵⁴ and the benzoate ion⁷⁰.

Conclusions

Thus, inhibitors of corrosion in acid solution can interact with metals and affect the corrosion reaction in a number of ways, some of which may occur

simultaneously. It is often not possible to assign a single general mechanism of action to an inhibitor, because the mechanism may change with experimental conditions. Thus, the predominant mechanism of action of an inhibitor may vary with factors such as: its concentration, the pH of the acid, the nature of the anion of the acid, the presence of other species in the solution, the extent of reaction to form secondary inhibitors and the nature of the metal. The mechanism of action of inhibitors with the same functional group may additionally vary with factors such as the effect of the molecular structure on the electron density of the functional group and the size of the hydrocarbon portion of the molecule. However, the mechanisms of action of a number of inhibitors have now been identified and are beginning to be understood on the molecular level.

Inhibitors in Near-neutral Solutions

The corrosion of metals in neutral solutions differs from that in acid solutions in two important respects (see Section 1.4). In air-saturated solutions, the main cathodic reaction in neutral solutions is the reduction of dissolved oxygen, whereas in acid solution it is hydrogen evolution. Corroding metal surfaces in acid solution are oxide free, whereas in neutral solutions metal surfaces are covered with films of oxides, hydroxides or salts, owing to the reduced solubility of these species. Because of these differences, substances which inhibit corrosion in acid solution by adsorption on oxide-free surfaces, do not generally inhibit corrosion in neutral solution*. Inhibition in neutral solutions is due to compounds which can form or stabilise protective surface films. The inhibitor may form a surface film of an insoluble salt by precipitation or reaction. Inhibitors forming films of this type include: (a) salts of metals such as zinc, magnesium, manganese and nickel, which form insoluble hydroxides, especially at cathodic areas, which are more alkaline due to the hydroxyl ions produced by reduction of oxygen; (b) soluble calcium salts, which can precipitate as calcium carbonate in waters containing carbon dioxide, again at cathodic areas where the high pH permits a sufficiently high concentration of carbonate ions; (c) polyphosphates in the presence of zinc or calcium, which produce a thin amorphous salt film. The mechanism of action of these inhibitors seems fairly straightforward⁸⁸. The salt films, which are often quite thick and may be visible, restrict diffusion, particularly of dissolved oxygen to the metal surface. They are poor electronic conductors and so oxygen reduction does not occur on the film surface; these inhibitors are referred to, therefore, as cathodic inhibitors. The mechanism of inhibition by polyphosphates is more complex, and the various theories of their action have recently been described by Butler⁸⁹.

Another class of inhibitors in near-neutral solutions act by stabilising oxide films on metals to form thin protective passivating films. Such inhibitors are the anions of weak acids, some of the most important in practice being chromate, nitrite, benzoate, silicate, phosphate and borate. Passivating

*Exceptions are organic compounds of high molecular weight, e.g. gelatine, agar and dextrin. Adsorption of these large molecules is partly effective in shielding the metal surface from reaction in neutral as well as acid solutions².

oxide films on metals offer high resistance to the diffusion of metal ions and the anodic reaction of metal dissolution is inhibited; thus these inhibitive anions are often referred to as *anodic* inhibitors, and they are more generally used than cathodic inhibitors to inhibit the corrosion of iron, zinc, aluminium, copper and their alloys, in near neutral solutions.

The conditions under which oxide films are protective on these metals in relation to inhibition by anions may be characterised in terms of three important properties of the oxide film (see also Sections 1.4 and 1.5):

1. The Flade potential, which is the negative potential limit of stability of the oxide film. At potentials more negative than the Flade potential the oxide film is unstable with respect to its reduction or dissolution, or both, since the rates of these two processes exceed that of film formation.
2. The critical breakdown potential, which is the positive potential limit of stability of the oxide film. At this potential and more positive potentials, the oxide film is unstable with respect to the action of anions, especially halide ions, in causing localised rupture and initiating pitting corrosion.
3. The corrosion current due to diffusion of metal ions through the passivating film, and dissolution of metal ions at the oxide-solution interface. Clearly, the smaller this current, the more protective is the oxide layer.

All of these three properties of the oxide films on metals are influenced by the anion composition and pH of the solution. In addition the potential of the metal will depend on the presence of oxidising agents in the solution. Inhibition of corrosion by anions thus requires an appropriate combination of anions, pH and oxidising agent in the solution so that the oxide film on the metal is stable (the potential then lying between the Flade potential and the breakdown potential), and protective (the corrosion current through the oxide being low).

Most of the information available on the mechanism of action of inhibitive anions relates to iron, which will be discussed in some detail, and followed by brief accounts of zinc, aluminium and copper.

Iron

The corrosion of iron (or steel) can be inhibited by the anions of most weak acids under suitable conditions⁹⁰⁻⁹². However, other anions, particularly those of strong acids, tend to prevent the action of inhibitive anions and stimulate breakdown of the protective oxide film. Examples of such aggressive anions are the halides, sulphate, nitrate, etc. Brasher⁹² has shown that, in general, most anions exhibit some inhibitive and some aggressive behaviour towards iron. The balance between the inhibitive and aggressive properties of a specific anion depends on the following main factors (which are themselves interdependent).

Concentration Inhibition of iron corrosion in distilled water occurs only

when the anion concentration exceeds a critical value⁹⁰⁻⁹³. At concentrations below the critical value, inhibitive anions may act aggressively and stimulate breakdown of the oxide films⁹². Effective inhibitive anions have low critical concentrations for inhibition. Brasher⁹² has classified a number of anions in order of their inhibitive power towards steel, judged from their critical inhibitive concentrations. The order of *decreasing* inhibitive efficiency is: azide, ferricyanide, nitrite, chromate, benzoate, ferrocyanide, phosphate, tellurate, hydroxide, carbonate, chlorate, *o*-chlorbenzoate, bicarbonate, fluoride, nitrate, formate. Thus, normally aggressive anions such as fluoride and nitrate may inhibit steel corrosion at sufficiently high concentrations.

pH Inhibitive anions are effective in preventing iron corrosion only at pH values more alkaline than a critical value. This critical pH depends on the anion, e.g. approximate critical pH values for the inhibition of iron or steel in about 0.1 M solution of the anion *increase* in the order: chromate⁹⁴, 1.0; azelate⁹⁵, 4.5; nitrite^{96, 97}, 5.0–5.5; benzoate^{98, 99}, 6.0; phosphate¹⁰⁰, 7.2; hydroxide⁹¹, ≈ 12 (not 0.1 M). The critical pH value for inhibition depends on the concentration of the inhibitive anion. In azelate⁹⁵ and nitrite⁹⁶ solutions, there are indications that the critical pH for inhibition decreases as the anion concentration increases. However, in benzoate solutions⁹⁹, increasing benzoate concentration displaces the critical pH to more alkaline values.

Dissolved oxygen concentration and supply Inhibition of the corrosion of iron by anions requires a critical minimum degree of oxidising power in the solution. This is normally supplied by the dissolved oxygen present in air-saturated solutions. Gilroy and Mayne¹⁰¹ have shown that the critical oxygen concentration for inhibition of iron in 0.1 M sodium benzoate (pH 7.0) is ≈ 0.3 p.p.m., considerably less than the air-saturated concentration of ≈ 8 p.p.m. As the oxygen concentration is reduced below this critical value, the rate of breakdown of the passivating oxide film increases. As the pH of 0.1 M sodium benzoate is reduced below 7.0, the critical oxygen concentration for inhibition increases¹⁰². The critical oxygen concentration for inhibition depends on the nature of the anion¹⁰¹. If the inhibitive anion possesses oxidising properties, e.g. chromate^{93, 103, 104}, nitrite⁹³, pertechnetate¹⁰⁴⁻¹⁰⁶, then the presence of dissolved oxygen may not be necessary for inhibition. The critical oxygen concentrations for good inhibitive non-oxidising anions are low¹⁰¹. If the dissolved oxygen concentration is increased above that of the air-saturated solution, the inhibition of iron corrosion is facilitated¹⁰², and inhibition may even be achieved in chloride solution¹⁰⁷. Similarly, increasing the oxygen supply to the iron surface by rapid stirring or aeration of the solution may favour inhibition, resulting in inhibition at lower critical anion concentrations^{98, 108}, and again inhibition in chloride solutions may be obtained¹⁰⁹. Addition of an oxidising agent may improve the efficacy of inhibitive anions, e.g. Mayne and Page¹¹⁰ have recently shown that the presence of hydrogen peroxide lowers the critical concentrations of sodium benzoate and sodium azelate required for inhibition of steel, and also lowers the critical pH values for inhibition.

Aggressive anion concentration When aggressive anions are present in the

solution, the critical concentrations of inhibitive anions required for protection of iron are increased^{108,111-116}. Brasher and Mercer¹¹²⁻¹¹⁵ have shown that the relationship between the maximum concentration of aggressive anion $C_{agg.}$ permitting full protection by a given concentration of inhibitive anion $C_{inh.}$ is of the form

$$\log C_{inh.} = n \log C_{agg.} + K$$

where K is a constant dependent on the nature of the inhibitive and aggressive anions, and n is an exponent which is approximately the ratio of the valency of the inhibitive anion to the valency of the aggressive anion. This relationship indicates a competitive action between inhibitive anions and aggressive anions and its significance will be discussed below. In general, the more aggressive the anion, the smaller the concentration which can be tolerated by an inhibitive anion. The order of tolerance¹¹⁵ of aggressive anions is, with certain exceptions, consistent with the order of aggressiveness of these anions as determined from their tendency to induce breakdown of the oxide film on iron in aerated solutions.

Nature of the metal surface The critical concentration of an anion required to inhibit the corrosion of iron may increase with increasing surface roughness. Thus, Brasher and Mercer¹¹² showed that the minimum concentration of benzoate required to protect a grit-blasted steel surface was about 100 times greater than that required to protect an abraded surface. However, surface preparation had little effect on the critical inhibitive concentrations for chromate¹¹³ or nitrite¹¹⁴. The time of exposure of the iron surface to air after preparation and before immersion may also affect the ease of inhibition by anions. There is evidence^{91,101,117} that the inhibition by anions occurs more readily as the time of pre-exposure to air increases. Similarly, if an iron specimen is immersed for some time in a protective solution of an inhibitive anion, it may then be transferred without loss of inhibition to a solution of the anion containing much less than the critical inhibitive concentration⁹¹.

Temperature In general, the critical concentrations of anions, e.g. benzoate^{108,112}, chromate¹¹³ and nitrite¹¹⁴, required for the protection of steel increase as the temperature increases.

Passivating Oxide Films

Studies of iron surfaces inhibited in solutions of anions have shown by several independent techniques, e.g. examination of *in situ* and stripped films by electron diffraction¹¹⁸⁻¹²⁴, cathodic reduction^{123,125,126} and ellipsometry¹²⁷, the presence of a thin film (thickness $\approx 3 \times 10^{-6}$ m to 5×10^{-9} m) of cubic iron oxide (Fe_3O_4 or $\gamma\text{-}Fe_2O_3$), which is rather similar to the air-formed oxide film¹²⁸⁻³⁰. Immersion of iron bearing its air-formed oxide film into solutions of inhibitive anions usually results in a thickening of the oxide layer^{125,131}, except at relatively low pH¹³². Oxide film growth on iron in inhibitive solutions of anions as well as in air, follows a direct logarithmic law, the rate constants being generally slightly greater in solution than

in air^{94, 127, 131, 133-136}. It is generally agreed that inhibition of the corrosion of iron by anions results from their effects on this oxide layer¹³⁷⁻¹⁴⁴. These effects are of several kinds, and they will now be discussed in relation to the theories of inhibition by anions. It seems probable, that there is no single mechanism of inhibition, but that a number of factors are involved, their relative importance depending on the nature of the anion and experimental conditions.

Uptake of Anions by Oxide Films

Early studies on oxide films stripped from iron showed the presence of chromium after inhibition in chromate solution¹⁴⁵ and of crystals of ferric phosphate after inhibition in phosphate solutions¹²¹. More recently, radio-tracer studies using labelled anions have provided more detailed information on the uptake of anions. These measurements of irreversible uptake have shown that some inhibitive anions, e.g. chromate^{94, 133, 136, 146, 147} and phosphate^{117, 148}, are taken up to a considerable extent on the oxide film. However, other equally effective inhibitive anions, e.g. benzoate^{149, 150} pertechnetate^{151, 152} and azelate¹⁵³, are taken up to a comparatively small extent. Anions may be adsorbed on the oxide surface by interactions similar to those described above in connection with adsorption on oxide-free metal surfaces. On the oxide surface there is the additional possibility that the adsorbed anions may undergo a process of ion exchange^{115, 117, 147}, whereby they replace oxide ions, which leave the oxide lattice for the solution. Adsorption and ion-exchange represent different aspects of the same process. However, it would be expected that an anion would be more firmly bound after ion exchange because of the greater interaction with neighbouring metal ions. Anions taken up by adsorption/ion exchange, e.g. phosphate¹¹⁷ and chromate¹⁴⁷, would be expected to be distributed fairly uniformly over the surface, though binding energies would vary with different types of adsorption site. There is considerable evidence that uptake of anions may also be concentrated into particles of separate phases located in the main oxide film, e.g. phosphate^{117, 121}, pertechnetate¹⁰⁵ and azelate¹⁵³. The formation of these particles of separate phase has been observed mainly when conditions are relatively unfavourable for inhibition, e.g. low pH¹⁵³, thin oxide film due to short air exposure¹¹⁷ and the presence of aggressive anions¹⁵⁴.

This evidence of the uptake of inhibitive anions into oxide films forms the basis of the 'chemical' or 'pore plugging' theory of inhibition, associated originally with Evans¹⁵⁵ *et al.* In this theory the rôle of the inhibitive anion is to promote the repair of weak points or pores in the oxide film, where corrosion has started, by reacting with dissolving iron cations to form insoluble products of separate phase, which plug the gaps. These insoluble products may contain the inhibitive anion either as a salt, e.g. phosphate¹²¹, or a basic salt, e.g. azelate¹⁵³, or as an insoluble oxide, e.g. Cr_2O_3 from chromate^{133, 145}. Precipitation of such solid products is favoured if the pH in the region of the pores does not become acid. Thus, on the basis of this theory, inhibition by anions such as phosphate, borate, silicate and carbonate, is enhanced by their buffer properties which serve to prevent a fall in pH in the anodic areas. Since ferric salts are usually more insoluble than

ferrous salts, the requirement of oxidising power in the solution for inhibition is explained as necessary for oxidation of ferrous to insoluble ferric compounds, either by dissolved oxygen or oxidising anions, e.g. chromate or nitrite.

There is undoubted evidence that pore plugging as described by this theory does occur, particularly when conditions are relatively unfavourable for inhibition. However, this theory does not provide a complete explanation of the action of inhibiting anions. Some inhibitive anions, e.g. azide⁹¹ and pertechnetate¹⁴⁰, do not form insoluble salts with ferrous or ferric ions. Furthermore, the pertechnetate ion has negligible buffer capacity¹⁴⁰. Oxidising power is not necessarily a criterion of inhibitive efficiency, e.g. permanganate rapidly oxidises ferrous ions to ferric, but is a poor inhibitor¹⁵⁶. Also, there is little correlation between the extent to which anions are incorporated into oxide films and their inhibitive efficiency¹¹⁷. The inhibitive action of anions on iron is soon lost after transfer of the metal from the anion solution to water. The behaviour^{111, 115} of iron in solutions containing mixtures of inhibitive and aggressive anions indicates that there is a competitive uptake of the inhibitive and the aggressive anions. These facts strongly suggest that the inhibitive effect of anions is exerted through a relatively labile adsorption on the oxide surface, rather than irreversible incorporation into the oxide film.

Effect of Inhibitive Anions on Formation of Passivating Oxide

Inhibitive anions can also contribute to the repair of weak points, pores or damage to the oxide film on iron by promoting the formation of a passivating film of iron oxide at such areas. This was put forward as a mechanism of action of inhibitive anions by Stern¹⁵⁷, who proposed that the formation of passivating iron oxide was easier in the presence of such anions (due to an increase in the rate of the cathodic process, arising from either reduction of an oxidising anion or acceleration of oxygen reduction) so that a greater equivalent anodic current would be available to more easily exceed the critical current density for passivation. Stern also suggested that inhibitive anions might facilitate the anodic process of oxide formation by reducing the magnitude of the critical current density or by making the Flade potential more negative. Subsequent work has shown that inhibitive anions affect mainly the anodic process. Thus in solutions of the oxidising inhibitive anions chromate^{103, 158}, nitrite^{158, 159} and pertechnetate¹⁰⁶, reduction of dissolved oxygen is the predominant cathodic process. There is evidence^{103, 160}, that some anions can increase somewhat the rate of oxygen reduction, but the effects do not appear sufficiently large to be significant. However, anodic polarisation studies^{158, 161-163} have shown that the critical current density for passivation is much smaller in the presence of inhibitive anions than aggressive anions. Comparing a number of inhibitive anions¹⁵⁸, the critical current densities for passivation have been found to increase in generally the same order as the inhibitive efficiencies decrease. In solutions of inhibitive anions^{158, 164}, as the pH becomes more acid the critical current density for passivation generally increases. In benzoate solution¹⁶⁴, the presence of dissolved oxygen has been shown to reduce considerably the critical current

density for passivation. However, in carbonate solution¹⁶³, dissolved oxygen has little effect. The effects of anions on the passivation reaction are related to their adsorption, since radiotracer measurements¹⁶⁵ during passivation of iron in solutions of sodium phosphate and sodium iodohippurate (a substituted benzoate) have indicated that the greater the adsorption of the anion on the active iron surface, the smaller the critical current density for passivation.

Brasher^{166, 167} has found that a steel specimen which has begun to corrode in a solution of an aggressive anion can be inhibited by addition of a non-oxidising inhibitive anion only if the potential has not become more negative than a certain value, termed the 'critical potential for inhibition'. This critical potential depends on the nature of the anion¹⁶⁷, and on the relative concentrations of inhibitive and aggressive anions in the solution, becoming more positive as the concentration of aggressive anion increases¹⁶⁸. The critical potential for inhibition has been related to the effects of potential on the adsorption of anions^{165, 168}, and is probably the potential at which adsorption of the inhibitive anion on the active corroding areas has the minimum value necessary to reduce the metal ion dissolution rate to such an extent that oxide film formation can occur. In pure benzoate or phosphate solutions, the critical potentials for inhibition (benzoate -0.28 V, phosphate -0.43 V) are close to the critical passivation potentials^{158, 164} for iron. This is a further indication that inhibition under these circumstances occurs due to the formation of passivating iron oxide at the corroding areas.

Effects of inhibitive Anions on the Dissolution of Passivating Oxide

The passivating oxide layer on iron should remain stable and protective provided its rate of formation exceeds its rate of dissolution. Dissolution of the outer layer of $\gamma\text{-Fe}_2\text{O}_3$ can occur in two ways. At potentials more positive than the Flade potential, dissolution occurs by passage of Fe^{3+} ions from the oxide surface into solution^{169, 170}. The effect of anions on the rate of this process has not been systematically studied, but there is evidence that the rates are considerably smaller in solutions of chromates⁹⁴ than of sulphate¹⁶⁹. However, the rates in sulphate are slightly less than in solutions of phthalate¹⁷¹, an inhibitive anion, which may be due to some complex formation. The dissolution rates in solutions of these anions decrease considerably as the pH increases. The thickness of the oxide film on iron also controls the Fe^{3+} dissolution rates, which decrease markedly as the oxide film thickness increases¹⁷⁰. Thus, under adverse conditions, i.e. relatively low pH, low inhibitive power of anions, low oxide thickness (especially at weak points in the film), on immersion of an iron specimen, an appreciable Fe^{3+} dissolution current could flow, which could depress the potential to the vicinity of the Flade potential. In this region, the rate of oxide dissolution increases¹⁷⁰, due to the onset of reductive dissolution^{101, 172}, leading to passage of Fe^{2+} ions into solution. The dissolving Fe^{2+} ions derive from the reduction of Fe^{3+} ions in the surface layer of $\gamma\text{-Fe}_2\text{O}_3$, by electrons supplied from the oxidation of metallic iron to form cations. Gilroy and Mayne¹⁰¹ have shown that the rate of reductive dissolution of the oxide film

on iron is faster in solutions of aggressive anions than in solutions of inhibitive anions. The rate of dissolution increases as the dissolved oxygen content decreases. Gilroy and Mayne have shown further¹⁷³ that the rates of oxidation in solution of Fe^{2+} to Fe^{3+} by dissolved oxygen are greater in the presence of inhibitive anions than of aggressive anions. They propose that a function of the inhibitive anion is to stimulate the oxidation by oxygen of any Fe^{2+} ions produced in the surface of the $\gamma\text{-Fe}_2\text{O}_3$ film, thus retarding its dissolution. These effects of anions on the reductive dissolution of the oxide film should correspond to effects on the Flade potential, i.e. a decrease in the rate of reductive dissolution should displace the Flade potential to more negative values, and vice versa. The effects of a number of anions at varying pH on the Flade potential have been described by Freiman and Kolotyrkin¹⁷⁴.

The reductive dissolution of the outer $\gamma\text{-Fe}_2\text{O}_3$ layer exposes the inner magnetite layer of the oxide film. In acid solutions (pH less than 4) the magnetite layer rapidly dissolves¹⁷⁵, but in near neutral solution it may be stable and protective, depending on the nature of the anion present and its concentration^{176,177}. The magnetite layer is stable in inhibitive solutions of anions, e.g. benzoate¹⁷⁷, carbonate¹⁶³, hydroxide¹⁶³, borate¹²⁶ (though not bicarbonate¹⁷⁷). The stability of the magnetite layer controls the inhibition of corrosion of iron when coupled to electronegative metals such as aluminium, zinc or cadmium¹⁷⁷.

Thus inhibitive anions can retard the dissolution of both the $\gamma\text{-Fe}_2\text{O}_3$ and the magnetite layers of the passivating oxide layer on iron. This has the dual effect of preventing breakdown of an existing oxide film and also of facilitating the formation of a passivating oxide film on an active iron surface, as discussed in the previous section.

Inhibitive Anions and Aggressive Anions

An important function of inhibitive anions is to counteract the effects of aggressive anions which tend to accelerate dissolution and breakdown of the oxide films. The relationships¹¹⁵ (mentioned above) between the concentrations of inhibitive anions and aggressive anions, when inhibition is just achieved, correspond to competitive uptake of the anions by adsorption or ion exchange at a fixed number of sites at the oxide surface. The effects of the valencies of the competing anions are generally consistent with the total charge due to anion uptake being constant. Iron surfaces protected in solutions of inhibitive anions rapidly begin to corrode on addition of aggressive anions or on transfer to distilled water. All these facts indicate that inhibitive anions overcome the effects of aggressive anions through participation in a reversible competitive adsorption such that the adsorbed inhibitive anions reduce the surface concentration of aggressive anions below a critical value.

The reasons why some anions exhibit strong inhibitive properties while others exhibit strong aggressive properties are not entirely clear. The principal distinction seems to be that inhibitive anions are generally anions of weak acids whereas aggressive anions are anions of strong acids. Due to hydrolysis, solutions of inhibitive anions have rather alkaline pH values and buffer capacities to resist pH displacement to more acid values. As discussed

above, both these factors are beneficial to the stability and repair of the oxide film. However, the primary difference between inhibitive and aggressive anions must arise from their effects on dissolution reactions at the oxide surface. For the various XO_4^{n-} ions, Cartledge^{140,143} considers that the difference between inhibitive and non-inhibitive anions is due to the contrasting internal polarity of the X^+-O^- bond creating different electrostatic interactions in the electrical double layer, thus affecting transfer of metal ions into solution. Another important factor is that the bonds formed between anions of weak acids and metal ions in the oxide surface are of a more coordinate character than those formed by anions of strong acids. The mechanism of dissolution of metal ions from the oxide surface is not well understood, but according to Heusler¹⁷⁰ it proceeds by the passage of $Fe(OH)^{2+}$ ions into solution. It seems likely that dissolution of other anion complexes will occur, and it would appear that dissolution of the more coordinately bonded complexes with inhibitive anions occurs less readily than that of the more ionically bonded complexes with aggressive anions. In addition, the electron transfer to the ferric ion in the coordinate bonds with inhibitive anions will tend to stabilise the ferric state against reduction to the ferrous state, making the oxide more resistant to reductive dissolution.

The inhibitive efficiency of anions tends to increase with size in a homologous series⁹¹, due probably to the increasing tendency to adsorption, and decreasing solubility of the ferric-anion complex.

Zinc

The effects of inhibitive and aggressive anions on the corrosion of zinc are broadly similar to the effects observed with iron. Thus with increasing concentration, anions tend to promote corrosion but may give inhibition above a critical concentration^{141,160,178}. Inhibition of zinc corrosion is somewhat more difficult than that of iron, e.g. nitrite^{179,180} and benzoate^{98,181,182} are not efficient inhibitors for zinc. However, inhibition of zinc corrosion is observed in the presence of anions such as chromate^{91,178,179}, borate¹⁷⁹ and nitrocinnamate^{91,179}, which are also good inhibitors for the corrosion of iron. Anions such as sulphate, chloride and nitrate are aggressive towards zinc and prevent protection by inhibitive anions^{141,160}. The presence of dissolved oxygen in the solution is essential for protection by inhibitive anions. As in the case of iron, pressures of oxygen greater than atmospheric or an increase in oxygen supply by rapid stirring can lead to the protection of zinc in distilled water¹⁸³. Inhibition of zinc corrosion occurs most readily¹⁸⁴ in the pH range of 9 to 12, which corresponds approximately to the region of minimum solubility of zinc hydroxide.

The ways in which inhibitive anions affect the corrosion of zinc are mainly similar to those described above for iron. In inhibition by chromate, localised uptake of chromium has been shown to occur at low chromate concentrations^{160,185} and in the presence of chloride ions¹⁸⁵. Thus under conditions unfavourable for inhibition, pore plugging occurs on zinc. Inhibitive anions also promote the passivation of zinc, e.g. passivation is much easier in solutions of the inhibitive anion, borate¹⁸⁶⁻¹⁸⁸, than in solutions of the non-inhibitive anions, carbonate and bicarbonate^{186,189}. A critical

inhibition potential, analogous to that on iron, has been observed for zinc in borate solutions¹⁴⁴. Thus inhibitive anions promote repair of the oxide film on zinc by repassivation with zinc oxide. The requirement of dissolved oxygen for inhibition indicates that the passivating oxide is stabilised at potentials more positive than the Flade potential by the reduction in dissolution rate due to the inhibitive anion. The passivating film is ZnO, which dissolves as divalent cations¹⁹⁰, and there is no evidence of reductive dissolution. Thus, on zinc the inhibitive anion presumably stabilises the oxide by formation of an adsorbed complex with the zinc ion, the dissolution rate of which is less than that of analogous zinc complexes with water, hydroxyl ions or aggressive anions.

Aluminium

When aluminium is immersed in water, the air-formed oxide film of amorphous γ -alumina initially thickens (at a faster rate than in air) and then an outer layer of crystalline hydrated alumina forms, which eventually tends to stifle the reaction¹⁹¹⁻¹⁹³. In near-neutral air-saturated solutions, the corrosion of aluminium is generally inhibited^{194, 195} by anions which are inhibitive for iron, e.g. chromate, benzoate, phosphate, acetate. Inhibition also occurs in solutions containing sulphate or nitrate ions, which are aggressive towards iron. Aggressive anions for aluminium include the halide ions^{192, 194-196}, F^- , Cl^- , Br^- , I^- , which cause pitting attack, and anions which form soluble complexes with aluminium¹⁹⁴, e.g. citrate and tartrate, which cause general attack. Competitive effects^{195, 197}, similar to those observed on iron, are observed in the action of mixtures of inhibitive anions and chloride ions on aluminium. The inhibition of aluminium corrosion by anions exhibits both an upper and a lower pH limit. The pH range for inhibition depends upon the nature of the anion¹⁹⁴.

In near-neutral and de-aerated solutions¹⁹⁴, the oxide film on aluminium is stable and protective in distilled water and chloride solutions, as well as in solutions of inhibitive anions. Thus the inhibition of aluminium corrosion by anions differs from that of iron or zinc in that the presence of dissolved oxygen in the solution is not necessary to stabilise the oxide film, i.e. the Flade potential is more negative than the hydrogen evolution potential. Lorking and Mayne^{194, 196} observed that inhibition of aluminium corrosion occurred only when the initial rate of dissolution of aluminium oxide in solutions of anions was less than a critical value. If this dissolution rate was decreased by presaturation of the solution with aluminium oxide, the corrosion of aluminium could be inhibited in normally aggressive solutions containing chloride or fluoride ions. The oxide film dissolves as Al^{3+} ions, the degree of hydrolysis and rate of dissolution depending on the pH¹⁹⁸⁻²⁰¹. There is no evidence of reductive dissolution. Thus, as with zinc, the inhibitive anions probably act by adsorption on to Al^{3+} ions in the oxide surface to form a surface complex, which has a low dissolution rate. The formation of surface compounds by anions on aluminium oxide has been discussed by Vedder and Vermilyea^{202, 203} in connection with the inhibition of hydration of anodic oxide films on aluminium. In corrosion inhibition by chromate ions, their interaction with the oxide film on aluminium has been

shown by Heine and Pryor²⁰⁴ to result in the formation of an outer layer of the film which is more protective due to its high electronic resistance and low dissolution rate. Chromate ions were also found to prevent the uptake and penetration of chloride ions into the aluminium oxide film^{204,205}.

Copper

Little work has been carried out on the mechanism of inhibition of the corrosion of copper in neutral solutions by anions. Inhibition occurs in solutions containing chromate⁹⁸, benzoate⁹⁸ or nitrite²⁰⁶ ions. Chloride ions^{206,207} and sulphide²⁰⁸ ions act aggressively. There is evidence²⁰⁹ that chloride ions can be taken up into the cuprous oxide film on copper to replace oxide ions and create cuprous ion vacancies which permit easier diffusion of cuprous ions through the film, thus increasing the corrosion rate.

Copper corrosion can also be effectively inhibited in neutral solution by organic compounds of low molecular weight, such as benzotriazole^{208, 210-212} and 2-mercaptobenzothiazole²⁰⁸. Benzotriazole is particularly effective in preventing the tarnishing and dissolution of copper in chloride solutions. In the presence of benzotriazole, the anodic dissolution reaction, the oxide film growth reaction and the dissolved oxygen reduction reaction, are all inhibited^{208, 212}, indicating strong adsorption of the inhibitor on the cuprous oxide surface.

Conclusions

The mechanism of action of inhibitive anions on the corrosion of iron, zinc and aluminium in near-neutral solution involves the following important functions:

1. Reduction of the dissolution rate of the passivating oxide film.
2. Repair of the oxide film by promotion of the reformation of oxide.
3. Repair of the oxide film by plugging pores with insoluble compounds.
4. Prevention of the adsorption of aggressive anions.

Of these functions, the most important appears to be the stabilisation of the passivating oxide film by decreasing its dissolution rate (Function 1). Inhibitive anions probably form a surface complex with the metal ion of the oxide, i.e. Fe^{3+} , Zn^{2+} , Al^{3+} , such that the dissolution rate of this complex is less than that of the analogous complexes with water, hydroxyl ions or aggressive anions. For iron only, the special mechanism of reductive dissolution enables the ferric oxide film to dissolve more easily as Fe^{2+} ions. Inhibitive anions may retard this process by catalysing the re-oxidation by dissolved oxygen of any Fe^{2+} formed in the oxide surface. Stabilisation of the oxide films by decrease of dissolution rate is also important with respect to repassivation by oxide formation (Function 2). The plugging of pores by formation of insoluble compounds (Function 3) does not appear to be an essential function, but is valuable in extending the range of conditions under which inhibition can be achieved. The suppression of the adsorption of

aggressive anions (Function 4) by participation in a dynamic reversible competitive adsorption equilibrium at the metal surface appears to be related to the general adsorption behaviour of anions rather than a specific property of inhibitive anions.

The relative importance of these functions also depends to a considerable extent on the solution conditions. Under favourable conditions of pH, oxidising power and aggressive anion concentration in the solution, Function 1 is probably effective in preventing film breakdown. Under unfavourable conditions for inhibition, localised breakdown will occur at weak points in the oxide film, and Functions 2 and 3 become important in repairing the oxide film.

Recent Developments

Recent developments in the mechanisms of corrosion inhibition have been discussed in reviews dealing with acid solutions²¹³⁻²¹⁷ and neutral solutions^{213, 214, 216, 218, 219}. Novel and improved experimental techniques²¹⁸, e.g. surface enhanced Raman spectroscopy²²⁰, infrared spectroscopy²²¹, Auger electron spectroscopy²²², X-ray photoelectron spectroscopy²²² and a.c. impedance analysis²²³, have been used to study the adsorption, interaction and reaction of inhibitors at metal surfaces.

Adsorption of Corrosion Inhibitors onto Metals

The bonding of adsorbed corrosion inhibitors onto metals has been described in terms of the concepts of 'hard-soft acid and bases'^{215, 224} and electrosorption valency²²⁵. Work has continued on the correlation of the effects of substituents in related molecules, e.g. aliphatic amines²²⁶, pyridines²²⁶⁻²²⁸, anilines²²⁹, benzoates^{230, 231}, anthranilates²³², thiophenes²³³, thioglycolic acids²³⁴ and benzotriazoles²³⁵, on inhibitive efficiencies with electron densities at functional groups. These studies have generally confirmed that, in both acid and neutral solutions, substituents increase the inhibitive efficiencies, probably because of stronger adsorption forces arising from increased electron density on the functional group due to a nucleophilic substituent, or the polar character of an electrophilic substituent. Considerable enhancement of adsorption and inhibition can occur with an inhibitor containing more than one functional group²³⁶ (particularly if chelation is possible^{237, 238}), or because of synergistic interaction of two inhibitors^{217, 239}. Inhibitive efficiencies have also been correlated with steric factors^{227, 240} and hydrophobicity^{241, 242}.

Mechanisms in Acid Solutions

The four mechanisms discussed above, of the action of inhibitors remain essentially unchanged. Further work on acetylenic alcohols has indicated that barrier films can form owing to crosslinking by hydrogen bonding and synergistic interactions²⁴³. Theoretical treatments of the electrochemical

mechanisms of inhibition have shown that the contribution of each mechanism can be evaluated from electrochemical data^{217, 244}. There is now considerable evidence that the corrosion of metals in acids can proceed also by a chemical mechanism²⁴⁵. Inhibitors can give different effects on the rates of chemical corrosion and electrochemical corrosion^{246, 247}.

Mechanisms in Near-neutral Solutions

The mechanisms of action of inhibitors which form salt films on metals have been reviewed²¹⁸.

Regarding inhibition of corrosion of iron and steel by anions, further evidence for anion incorporation into oxide films has been obtained using radiotracers²⁴⁸ and Auger electron spectroscopy²⁴⁹. Support for the pore-plugging mechanism has been given by autoradiography studies²⁴⁸, which have demonstrated that in inhibitive solutions containing carboxylate anions, the extent of localised uptake of the anion decreases with increasing pH and increasing inhibitive efficiency of the anion.

The anodic passivation of iron has been shown^{216, 219, 250-254} to involve the formation of an oxide of lower valency state, possibly containing the anion, before the formation of the ferric oxide film. The effects of anions on these processes have been discussed in relation to the role of metal ion-anion complexes^{250, 252, 254}. Inhibitive anions may be divided into two main types²¹⁶. Type I anions, which include particularly carboxylates such as benzoate²³⁰, phthalate^{230, 255, 256} and acetate²⁵⁷, have little or no inhibitive effect in deaerated solutions in retarding active dissolution and facilitating passivation. Dissolved oxygen above a critical concentration produces strong synergistic inhibitive effects, owing probably in part to the more alkaline pH produced at the metal surface by oxygen reduction^{216, 258}. Type II anions, which include the more effective inhibitors, nitrite²⁵⁹, chromate²⁵², molybdate^{252, 260}, substituted benzoates^{230, 231}, phenylanthranilates²³², have inhibitive properties in deaerated solution. The role of dissolved oxygen is then to act mainly as a redox system. The effects of inhibitive anions on the dissolution of the passivating oxide films are analogous^{261, 262}.

Recent developments have also been reported in the inhibition of zinc²³⁸, aluminium^{263, 264} and copper^{220, 265}.

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17.4 Boiler and Feed-water Treatment

Introduction

The explicit aims of boiler and feed-water treatment are to minimise corrosion, deposit formation, and carryover of boiler water solutes in steam. Corrosion control is sought primarily by adjustment of the pH and dissolved oxygen concentrations. Thus, the cathodic half-cell reactions of the two common corrosion processes are hindered. The pH is brought to a compromise value, usually just above 9 (at 25°C), so that the tendency for metal dissolution is at a practical minimum for both steel and copper alloys. Similarly, by the removal of dissolved oxygen, by a combination of mechanical and chemical means, the scope for the reduction of oxygen to hydroxyl is severely constrained.

Deposit control is important because porous deposits, under the influence of heat flux, can induce the development of high concentrations of boiler water solutes far above their normally beneficial bulk values with correspondingly increased corrosion rates. This becomes an increasingly important feature with increase in boiler saturation temperature. In addition, deposits can cause overheating owing to loss of heat transfer. Finally, carryover of boiler water solutes, which can be either mechanical or chemical, can lead to consequential corrosion in the circuit, either on-load or off-load. Material so transported can result in corrosion reactions far from its point of origin, with costly penalties. It is therefore preferably dealt with by a policy of prevention rather than cure.

All of these factors need to be taken into account when defining a tolerable boiler and feedwater regime for any given plant. This has been done, for example, in BS 2486 (BSI, 1968) and by various other bodies (see Section 5.5).

With increasing boiler operating pressure, considerations of purity become even more important. High-pressure utility boilers, whilst in the main operating at a few percent make-up, are extremely sensitive to contaminant ingress, so that high-purity feed-water is essential. Above about 40 bar, complete demineralisation is therefore virtually mandatory, with the result that scaling due to hardness salts is impossible, barring inadvertent cooling water ingress due to, for example, condenser leakage, rotary air pump

suckback, or water treatment plant malfunction. However, carryover of solutes in steam becomes increasingly important. This can occur either mechanically (in its worst form as priming) or chemically. In the latter case, substances become distributed between steam and water in a ratio determined by the temperature. Material carried over and subsequently deposited may cause a number of problems elsewhere in the steam/water circuit. Assuming however, that appropriate water treatment has been arranged, the treated water, although unlikely to form scale, and with a greatly diminished tendency to carryover, nevertheless may still cause corrosion unless the quality is further adjusted. This is done by additions and/or removals of substances.

Fundamental Considerations

Water Quality

The raw water available for any given installation will be of acceptable quality only rarely, and some degree of purification and adjustment will usually be needed. Following widely accepted usage we shall refer to the purification, i.e. the removal of undesirable constituents, as 'treatment' and the adjustment of quality or suitability, by, for example, alkalisation or deoxygenation, as 'conditioning'. Whilst a detailed consideration of methods of water treatment would be out of place here, nevertheless some brief discussion will be given as an aid to understanding the scope for corrosion control. Raw waters can be generally divided into four categories as follows:

1. *Well water*. This is rain water which has percolated through various strata until it enters an underground aquifer. Well water usually contains dissolved calcium and magnesium salts, but is low in organic matter owing to natural filtration.
2. *Upland surface water*. This is low in hardness salts having run over impervious rocks but will often be high in organic matter, i.e. fulvic and humic acids.
3. *Clean rivers*. These originate from upland surface waters, but contain more organic matter and also silt.
4. *Industrial rivers*. These are essentially re-used waters and contain, in addition to those constituents originally present, sewage and industrial wastes. A typical analysis of each of these water categories is presented in Table 17.2.

Table 17.2 Typical analysis of water categories

<i>Constituent</i>	<i>Water category</i>			
	<i>Well</i>	<i>Upland surface</i>	<i>Clear river</i>	<i>Industrial river</i>
Alkalinity (mg kg ⁻¹ CaCO ₃)	200	10	100	150
Calcium (mg kg ⁻¹ CaCO ₃)	90	12	100	250
Magnesium (mg kg ⁻¹ CaCO ₃)	120	5	50	100
Sodium (mg kg ⁻¹ CaCO ₃)	20	8	50	160
Chloride (mg kg ⁻¹ CaCO ₃)	10	10	50	130
Sulphate (mg kg ⁻¹ CaCO ₃)	20	5	50	230
Total organic carbon (mg kg ⁻¹ C)	0.2	5	8	15

Treatment of waters for boiler feed For most boilers, then, raw water from any of the above sources will require treatment followed by appropriate conditioning. In simple, low pressure plants, precipitation of the hardness salts, e.g. by lime or lime/soda, will be adequate.

For a wide range of low and intermediate pressure plant, base-exchange is applied. In this process, the potential scale-forming salts of calcium and magnesium are replaced by the equivalent sodium salts. This is achieved by passing the raw water through a bed—originally of a naturally occurring zeolite but now of a synthetic substitute—in which the exchange of unwanted for acceptable ions occurs. Periodic regeneration is necessary by passing brine through the bed. Whilst softened, i.e. rendered non-scaling, by this process, the water is corrosive owing to the presence of carbon dioxide, and in addition the solids content is undiminished. The corrosivity may be alleviated by conditioning, but the solids content becomes a constraining factor with increasing boiler pressure. Some means of lowering the solids content is therefore needed in many instances. Distillation was formerly extensively practised and is still viable in many situations. Increasingly, however, ion exchange is used.

Ion exchange is analogous to base exchange and can be used for the removal of either cations or anions. Cations are replaced by hydrogen ions and anions by hydroxyl ions. Again, regeneration is required, this being most conveniently achieved in the UK with sulphuric acid for cation resins and sodium hydroxide for anion resins. For most modern high-pressure boiler plants ion exchange forms the basis of the water treatment plant.

As many natural waters are coloured and turbid, and contain suspended solids (silt, clay etc) as well as organic matter, some pretreatment is necessary before ion-exchange as these impurities adversely affect resin performance and lead to lower water quality and higher operating costs. Pretreatment usually comprises coagulation/flocculation followed by settlement and filtration. Coagulation is often achieved by adding aluminium sulphate and, after subsequent flocculation etc, the suspended solids content of the water leaving the pretreatment plant should be less than 2 mg/kg. The water is then usually filtered through deep sand to provide an effluent of <0.2 mg/kg which is then fed to the ion-exchange plant proper. This, typically, would comprise a cation unit, a scrubbing tower for carbon dioxide removal, an anion unit, and a mixed bed (see Fig. 17.1).

Cation units usually contain a sulphonic acid resin whilst anion resins fall into the two main categories of strongly basic, with quaternary ammonium groupings and weakly basic, with tertiary amine groups. The final unit is the mixed bed in which, by a mixture of cation and anion resins in the same vessel, the effect is achieved of a multiplicity of separate cation and anion units. Resin separation is necessary for regeneration purposes. Considerable improvements in water quality are obtainable by these means.

The major chemical problem met in ion-exchange practice is the fouling or poisoning of the anion resins by organic matter. The various counter measures deployed include: pre-flocculation, oxidation of the organic material, the use of specially developed resins, and treatment of the fouled resins by brine and/or hypochlorite.

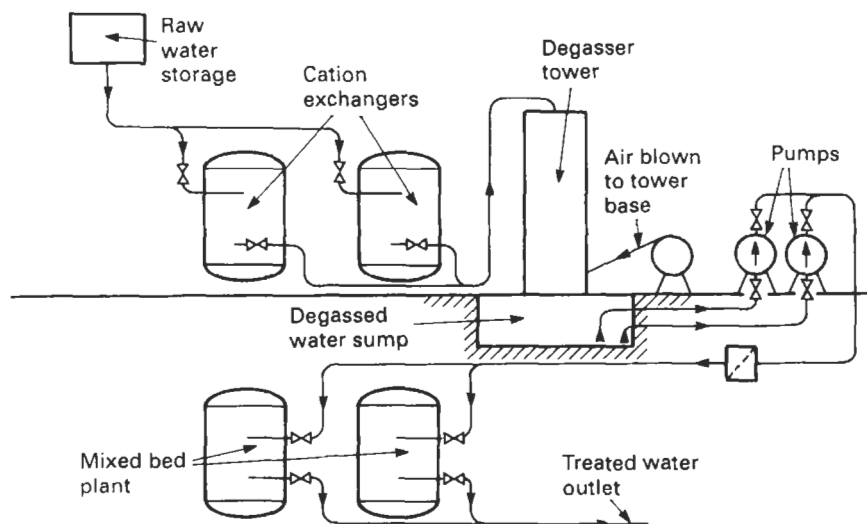


Fig. 17.1 Diagram of demineralisation plant

Condensate purification In some boiler systems the condensate returning is retreated using ion exchange to minimise corrosion and deposit accumulation. This particularly applies to once-through boilers (mainly nuclear) where there may be no water/steam separator and perhaps limited facilities for blow-down. Additionally, some high heat-flux boilers (oil-fired) have been fitted with condensate polishing plant (CPP).

The quality of water demanded from a CPP depends on the power plant which it services. An indication of the qualities demanded are given in Table 17.3.

Table 17.3 Water qualities demanded from condensate polishing for power plant

	AGR	PWR
Sodium ($\mu\text{g/kg Na}$)	< 2	< 0.5
Chloride ($\mu\text{g/kg Cl}$)	< 2	< 0.5
Sulphate ($\mu\text{g/kg SO}_4$)	< 2	< 0.5
Conductivity ($\mu\text{S/cm at } 25^\circ\text{C}$)	< 0.08	< 0.07

AGR, advanced gas-cooled reactor
PWR, pressurised water reactor

Basis of pH control

Essentially, the pH is controlled to suppress the hydrogen evolution cathodic reaction. The Pourbaix Diagram for iron indicates that high pH values as well as low values may lead to corrosion. The construction of these diagrams for higher than ambient temperatures^{1,2} shows how the area of the alkaline zones increases considerably under boiler conditions, so that the risk of corrosion is correspondingly higher. Many feed systems contain copper alloys,

as well as steel and, as the optimum pH values for the two materials differ, a compromise value has to be selected, values in the range 8·8–9·2 being suitable.

Some waters tend to become acidic owing, for example, to the hydrolysis of magnesium salts at elevated temperatures. Additions of alkali are needed to control the pH, and these may be required at more than one location in the system. As we have seen, initial design/economic considerations will show which quality of water to use as feed. Then, initially, some feed-line dosage will be required—solid alkalis for low-pressure plant, volatile alkalis for higher pressure boiler systems. Additional dosing to the boiler will also be desirable in some cases. However, once the system has done its work, e.g. by passing through a turbine, it becomes ‘condensate return’ and goes to supplement the feed-water. The amount of condensate return can range from nil to >99·5%, depending upon the type of plant.

Solid alkalis Solid alkalis may be used, in principle, for the corrosion control of drum boilers at all pressures but other factors, e.g. carryover or ‘hide-out’ a (reversible disappearance from solution on-load), may preclude them in some cases. However, they are used for feed-line treatment only in lower pressure plant where the boiler has increased tolerance to the higher solids burden which their use entails. Sodium hydroxide or, at very low pressures, sodium carbonate, (which is hydrolysed to the hydroxide at boiler temperatures) have been used, as have potassium and lithium hydroxides and various phosphate mixtures. (For a comparison of various alkalis for this purpose see Reference 3.)

The extent of feed-line dosage, and to some extent, its type, is influenced by the amount of make-up water required by the plant. This is the quantity of water which has to be added to the feed-water to replace that either taken from, or lost in, the cycle. The amount of make-up varies with the type of plant from 100% to less than 1%. With 100% make-up, solid alkali dosing would lead to the need for heavy and costly blow-down—increasingly so with the higher pressures owing to the greater amount of heat in the water. In contrast, in the boiler, as opposed to the feed system, solid alkalis are suitable for pH adjustment as long as they are properly controlled. Thus, on the one hand, if the concentration is too high (e.g. above 5 mg/kg NaOH at 160 bar), the sodium hydroxide carried over with the steam presents some risk to the circuit. On the other hand, in some boilers, solid chemicals are subject to hide-out. If kept within proper limits, however, solid alkalis have the advantage over volatile agents when strong acids are present in the boiler.

Organic bases Whilst for low-pressure situations, solid alkalis are acceptable for feed-line dosage, these become increasingly less desirable with higher pressures as boiler water requirements become increasingly stringent. An important control parameter is the dissolved solids content of the feed and boiler water (measured in terms of the electrical conductivity). If this is too great, blow-down requirements will be expensively high or the concentrations of sodium hydroxide and other solutes may increase to unacceptable levels with the risk of corrosion. This risk may to some extent be avoided by the use of organic bases for pH control. Their volatility prevents the development of high concentrations in the boiler and extends their protective effect

Table 17.4 Properties of amines

	Steam water partition		pK_b values		
	100°C	200°C	50°C	100°C	200°C
Ammonia	14	7.0	4.7	4.9	5.0
Cyclohexylamine	2.0	25	3.4	3.8	4.7
Morpholine	0.4	1.5	5.5	5.2	5.6
AMP ^a	0.4	0.9	4.3	4.3	5.0

^a2-amino-2-methyl-1-propanol. From Title and Kingerley⁴

throughout the steam/water circuit. At the same time, their weakly basic nature means that excessively high alkalinities cannot be achieved.

Various amines find application for pH control. The most commonly used are: ammonia, morpholine, cyclohexylamine, and, more recently AMP (2-amino-2-methyl-1-propanol). The amount of each needed to produce a given pH depends upon the basicity constant, K_b , and values of this are given in Table 17.4. The volatility also influences their utility and their selection for any particular application. Like other substances, amines tend towards equilibrium concentrations in each phase of the steam/water mixture, the equilibrium being temperature dependent. Values of the distribution coefficient, K_p , are also given in Table 17.4. These factors need to be taken into account when estimating the pH attainable at any given point in a circuit so as to provide appropriate protection for each location.

As feed systems usually contain copper alloys, the use of amines for their protection may seem somewhat strange as copper is prone to attack in ammonia/carbon dioxide/oxygen environments, with the formation of complex cupric or cuprous compounds. The requisite degree of protection can be achieved, however, by maintaining the concentrations strictly within the acceptable target range.

In some systems where condensate returns form part of the feed-water, the returned condensate may be considerably contaminated by, for example, air, carbon dioxide, possibly by process liquors, cooling water, perhaps by oil, as well as by products of corrosion of the system. Corrosion control in such systems can be difficult in view of the varying pattern and nature of the impurity ingress. For example, this can pose problems in providing suitable dosage to cope with the varying quantities of air ingress which accompany unplanned load changes on a plant throughout the day.

Filming amines In such situations, one approach is to use the filming type of amine, of which octadecylamine is the most common example. This, and related substances, forms a barrier on the internal surfaces of the feed system offering some protection against corrosive attack.

Filming amines are of a wax-like consistency and require dispersion before introduction to the system. Particular care is needed when starting the dosage in case agglomerates formed from the amine, and debris (crud), cause blockage.

An advantage of filming amines over neutralising amines is their relative independence of the concentration of corrosive substances. About 1–2 mg/kg of filming amine are usually adequate. This non-stoichiometric

behaviour is therefore of particular benefit in condensate return lines where large ingress of contaminant can occur.

Deoxygenation

Basis of deoxygenation The predominant cathodic reactions accompanying corrosion processes in aqueous solution are hydrogen evolution and dissolved oxygen reduction. With increasing pH, particularly above about 3 relative to 25°C the latter plays an increasingly important part, provided that sufficient oxygen is present. Deoxygenation therefore offers an important means of corrosion control.

The solubility of oxygen in water is influenced by several factors but, generally, most waters contain, at equilibrium, about 8 mg/kg at 25°C, although supersaturation may increase this considerably. Some indication of the amount of dissolved oxygen relevant in different situations is shown, on the one hand, by the value of 0.1 mg/kg found in central heating systems⁵ and, on the other hand, by the value of 0.005 mg/kg specified by most users of large boilers as the upper limit at the economiser inlet (see Section 5.5).

Deoxygenation can be achieved by mechanical and/or chemical means. Both methods are commonly used on conjunction, the chemical reagents being employed as 'scavengers' for the residual amount of oxygen left after mechanical treatment.

Mechanical/thermal deoxygenation A substantial amount of deoxygenation can be achieved by mechanical or thermal means. At 1 bar, for example, whilst the equilibrium concentration of dissolved oxygen in water is 8 mg/kg at 25°C, the figure is nearly zero at 100°C. Merely heating, therefore will decrease the oxygen content of the water by expelling it into the vapour phase. In practice, vapour, along with its oxygen burden has to be removed to prevent the reverse reaction.

Early types of equipment for this purpose include the vacuum deaerator, in which the water to be treated was introduced at high temperature into an evacuated atmosphere with a steam ejector operating in the vapour space. The residuals of oxygen attainable with the vacuum deaerator were limited to about 0.03 mg/kg, owing to the prevalent partial pressure of oxygen in the vapour phase. Lower residuals can be achieved by introducing another gas into the vapour phase and in boiler practice, this is conveniently provided by steam. By these means, the equipment can be operated at above ambient pressure, with concomitant advantages in respect of the lower solubility of oxygen in the liquid phase.

Pressure deaerators also serve as additional feed-water heaters. These are located in the pre-boiler system of a power plant between the low- and high-pressure heater trains. Residual oxygen concentrations of as low as 0.005 mg/kg O₂ are achievable by their use. The requirements for deaeration vary widely and are dependent upon the type of installation they are designed to serve. In central heating systems, make-up is minimal, provided that 'good housekeeping' limits the extent of leakage from the system and its consequential replacement by aerated make-up. Usually, therefore, no deaeration is applied. With low-pressure plant, either there may be no specific deaeration stage, or, perhaps, a vacuum deaerator. With

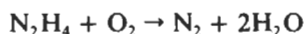
high-pressure plant, preliminary thermal/mechanical deaeration is essential, and a pressure deaerator is advisable.

In power generating practice, during steady-load operation, the scope for ingress of air is limited to leakage into those parts of the plant working at less than ambient pressure, i.e. the low pressure turbine and condenser, along with the air present in the small amount (about 1%) of make-up water. However, in variable-load operation, air ingress during shutdown periods, together with the large amounts of water used during run-ups, necessitate the use of auxiliary deaerating equipment, e.g. immersion heaters in the off-load plant and, perhaps, nitrogen sparging etc (see Section 4.7).

With lower pressure plant, when thermal deaeration may be rudimentary or even absent, reliance is placed on chemical means which, for higher pressure plant, play a complementary, but none the less important, role.

Chemical deoxygenation Tannins have been used traditionally for chemical deoxygenation and are still fairly effective for low-pressure plant. Sodium sulphite is also still used extensively in the same range. This reacts with oxygen to form the sulphate. Where sulphate is required in solution for other purposes, e.g. as a palliative against caustic cracking (see Section 4.2), the treatment clearly has some additional value, but, otherwise, the increase in dissolved solids content of the water due to its use may be undesirable. In addition, depending upon the boiler operating pressure and make-up rate, there may be some formation of acidic compounds, e.g. sulphur dioxide and hydrogen sulphide, which may cause corrosion (particularly) of the copper alloys of the circuit as well as introducing some imbalance into the chemical control⁶.

Hydrazine has the advantage that its use does not increase the dissolved solids content of the boiler water. The products both of its reaction with dissolved oxygen and of its decomposition are gaseous or liquid:



or, higher temperatures:



As a base, hydrazine will tend to increase the pH of the system. At ambient temperatures, the basicity of hydrazine is about one-tenth of that of ammonia, but with increasing temperature the disparity diminishes.

Hydrazine is conventionally added in an amount equivalent to at least 100% of the dissolved oxygen content. In principle, additions should be made after thermal deaeration to economise on reagent usage, but in practice in some cases more thorough scavenging is found to result if hydrazine is added before the deaerator. This may reflect the kinetic aspects of the reaction with oxygen.

Catalysis plays an important part in the hydrazine/oxygen reaction. Copper salts were formerly added for this purpose, but in recent years certain organic substances, e.g. quinhydrone, have been employed and a number of proprietary 'activated hydrazines' have been available. These are useful at low temperatures; above 150°C scavenging rates with normal hydrazine are such that no great benefit is achieved by their use.

In recent years, possible alternatives to hydrazine have been suggested, and some have been used on plant. These include: carbohydrazide ($\text{NH}_2\text{NHCONHNH}_2$), derivatives of hydroxylamine, e.g. diethyl hydroxylamine ($\text{HON}(\text{C}_2\text{H}_5)_2$), ketoximes, and erythroic acid (isoascorbic acid). These are usually faster scavengers than hydrazine or activated hydrazine⁷.

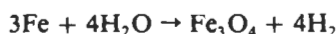
NOLC In certain special circumstances, rather than removing oxygen, deliberate additions of it have been found to be beneficial for combating corrosion provided that adequate control is maintained. In particular, the conductivity of the feed-water must be kept below $0.2 \mu\text{S}/\text{cm}$ at 25°C ⁸. The conditions are 'neutral water with oxygen and low conductivity'—hence the term 'NOLC'. The low conductivity requirement effectively limits the use of the method to once-through boilers. Oxygen is added either directly as such, or as hydrogen peroxide, and either at the economiser or, depending upon circumstances, earlier in the circuit.

With oxygenated regimes, the preferred oxide formed is haematite, instead of magnetite, and in addition thinner layers are found.

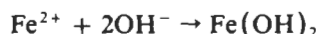
Mixed conditioning has also been used. In this, one part of the circuit (usually the low-pressure system) is dosed conventionally, e.g. with hydrazine/ammonia, whilst the high-pressure system is subjected to oxygenated conditions.

Boiler Corrosion: Laboratory Studies

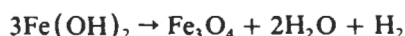
The prime reaction in boiler corrosion is the formation of magnetite and hydrogen from iron and water:



This is considered, however, to proceed in two stages, i.e. the initial production of ferrous hydroxide:



and is subsequent decomposition to magnetite and hydrogen (the Schikorr reaction):



Studies by Sweeton and Baes⁹ showed that this can be generalised into the reaction:



This implies that, given an adequate concentration of hydrogen, magnetite can be redissolved, and Berge *et al.*¹⁰ demonstrated that this is indeed so.

In the absence of sufficient hydrogen, the solubility of magnetite is markedly temperature dependent, which provides an explanation for some of the problems in high-temperature circuits. Most studies in boilers relate to high temperatures. Thus the work of Bloom¹¹ and of Potter and Mann¹² has reproduced the types of corrosion found in high-pressure boilers. The relationship between corrosion rates and iron solubility and pH are given in Fig. 17.2. Note that the pH range about the neutral point (relative to 300°C

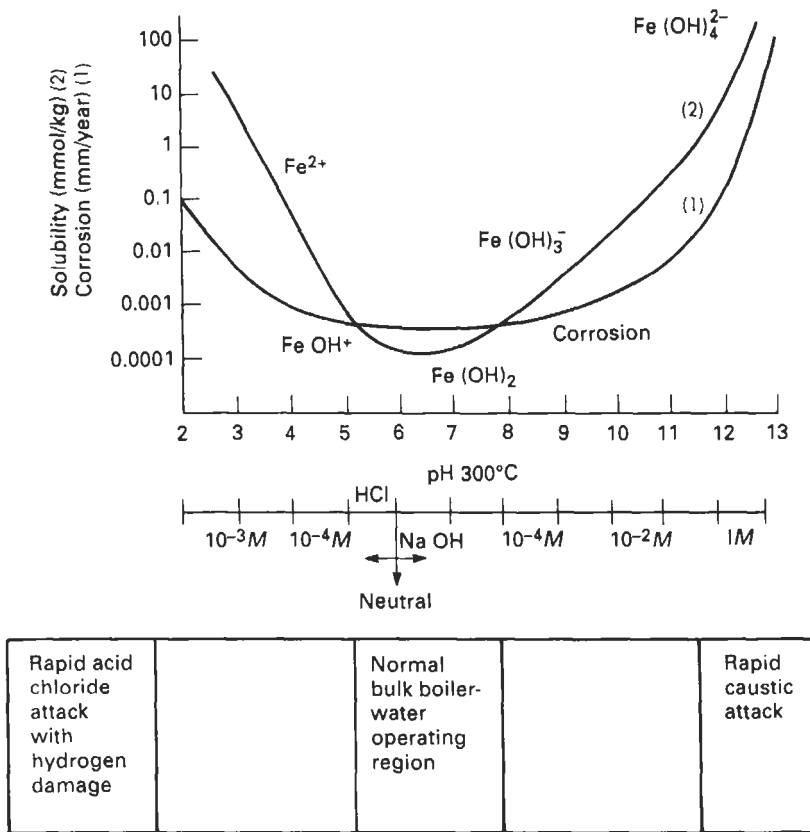
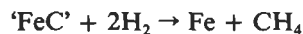


Fig. 17.2 Correlation between mild steel corrosion and magnetite solubility (by permission of G. M. W. Mann)

in the Figure), corresponding to the target ranges for good boiler-water practice, indicates modest corrosion rates. Excursions from neutral in either direction lead to increasingly severe attack, so that typical tube-wall thicknesses will be consumed in drastically short times, and faster in acids (100s of hours) than in alkalis (months). It should be noted that (in terms of tube integrity) acidic become more hazardous than alkaline solutions at lower concentration factors*—about 10^3 for acids and 10^4 to 10^5 for alkalis. In addition, Fig. 17.2 shows that with increasing acidity, the risk of hydrogen damage increases. By this mechanism, hydrogen generated by the corrosion process, attacks iron carbide in the steel:



and so transforms it into a material that does not possess the high-temperature strength required for boiler tube integrity. In addition, at high

*Concentration factor: the ratio of concentration locally to that in the bulk solution.

corrosion rates, the methane produced cannot diffuse out of the steel and high internal stresses develop which blow the steel apart. The rate of hydrogen damage is far higher than that of the corrosion process at boiler temperatures so that tubes with, say, 0.5 mm of corrosion damage may suffer hydrogen damage to the extent of, say, 5 mm and, in consequence, fail by brittle fracture.

Mechanistically, in approximately neutral solutions, solid state diffusion is dominant. At higher or lower pH values, iron becomes increasingly soluble and the corrosion rate increases with the kinetics approaching linearity, ultimately being limited by the rate of diffusion of iron species through the pores in the oxide layer. In more concentrated solutions, e.g. pH values of less than 3 or greater than 12 (relative to 25°C) the oxide becomes detached from the metal and therefore unprotective¹³. It may be noted that similar Arrhenius factors have been found at 75°C¹⁴ to those given by extrapolation of Potter and Mann's data from 300°C.

On plant there is significant transport of corrosion product oxide ('crud') from the feed and return lines. This can be the dominant factor, and overall the accumulation rate is effectively linear. It should be emphasised that corrosion of the type found in operating plant can only be reproduced in the laboratory by employing far higher concentrations (1 000 to 100 000 times) than those existing in bulk solution in practice. Interpretations therefore invoke the concept of concentration mechanisms.

Concentration Mechanisms

The three principal concentration mechanisms postulated as being responsible for on-load corrosion processes by Mann³ are dry-out, concentration in crevices, and concentration in porous deposits. (Clean boiler tube surfaces on which high-pressure water is boiled under forced convection do not develop concentration factors of more than about two.)

Baum¹⁵ has reviewed the theory and the laboratory, rig, and plant experience which has led to the current views on concentration mechanisms. Essentially, interpretation is based on the difference between heat transfer at certain localised sites of the tube and that at the free surface. In normal boiling, the removal of steam from the surface leads to its direct replacement by liquid, so that accumulation of solutes does not occur to any appreciable extent. However, in certain cases, principally those three listed above, where there is an inadequate supply of water to the surface for boiling to be maintained, steam preferentially forms. Consequently, solute is deposited and accumulates with the formation of highly concentrated solution (10^3 – 10^5 that in the bulk).

In the dry-out mode of concentration, the steam blanket causes the tube to become superheated, so that the temperature rises in proportion. In the second mode of concentration, i.e. at crevices, it arises initially because the confined space impedes coolant ingress so that the liquid component is impoverished, and insoluble species are precipitated. The deposit causes a rise in temperature and steam blanketing follows, as described above.

In the third common mode, wick-boiling occurs in the pores of the water-side deposit and produces increasingly concentrated solutions at the

deposit/tube interface owing to the relative impoverishment of the supply of liquid, and its resultant inability to exert sufficient cooling of the surface.

In these ways, then, concentration factors of up to five orders of magnitude may be developed, depending upon the circumstances. Despite much work in this area, theory has not yet developed to the stage where accurate predictions can be made reliably, but the state of the art is such that semi-quantitative assessments can be of considerable value in interpreting occurrences.

Feed-System Corrosion

General

Feed system problems may become apparent by failures at the immediate site of corrosion or indirectly, for example by the appearance of corrosion products in the form of deposits either in the feed or even the boiler system, leading to the blockage of instrument tapping points, sampling lines, blow-down lines etc., by the falling off in efficiency of the feed-heating plant, or by the removal of unduly large amounts of material on chemical cleaning. These may, be due to corrosion and/or scaling. Whilst operational needs may dictate that the immediate requirements are to remove the deposit and repair the failure, in the longer term it is equally important to identify and eradicate the root cause. This may prove to be, for example a water treatment plant malfunction, or ingress of air, or a temporary inadequacy of conditioning chemicals. Any of these would call for an increased degree of scrutiny in the monitoring procedures. In more chronic cases, a decision to upgrade the purity of the feed-water may be required, to use a different alloy or to change an operational procedure.

Both iron- and copper-based alloys are corroded more easily on either side of the neutral pH band. In low pH conditions e.g. due to carbon dioxide, the acidic environments attack the alloys readily, causing damage both at the points of initial corrosion and perhaps, consequentially, further along the system, by screening the surface with corrosion products and permitting the development of differential aeration cells.

A similarly undesirable situation is brought about in unduly alkaline solutions caused by the indiscriminate use of amines which may lead to high dissolution rates of copper from its alloys owing to complex formation. The standards discussed in Section 5.5 are aimed at avoiding these undesirable situations.

Erosion-Corrosion

There has been renewed interest over the last few years in erosion-corrosion, i.e. essentially 'velocity-assisted corrosion' since it appeared in the feed systems of certain nuclear plant. This prompted extensive experimental investigations¹⁶. Erosion-corrosion is influenced by many factors—chemistry, flow, temperature, heat flux, and whether one or two phases exist. It also varies with the material, resistance increasing from mild steel, through 1% Cr-Mo to 2% Cr-Mo.

Geometric factors, as might be expected, also influence the situation. High turbulence exerts an adverse effect, whilst a pH increase in the range 8.5 to 9.5 is beneficial. Dissolved oxygen concentration is also important, protection increasing with increasing oxygen content, in contrast with most forms of corrosion. The 'phase' stripping of dissolved gases has been claimed to be harmful. Temperatures of 140–150°C are the peak of bad conditions on a logarithmic wastage scale.

Boiler Waters

General Considerations

In boiler water practice the three main aims that must always be borne in mind are to minimise corrosion, deposition, and the carryover of boiler water solutes in steam. Increasing operating pressure of a boiler greatly affects the relative importance of these three aspects. For example, in a domestic central heating system, raw water may be acceptable, depending upon its source. From the initial charge of water, a small amount of scale will form and some slight corrosion will occur as the dissolved oxygen content of the water is consumed. If there is not an unduly large amount of make-up, there may be little more corrosion after this initial period. However, systems requiring substantial quantities of make-up generate more magnetite, and chemical dosage to decrease this may be desirable, perhaps in conjunction with water treatment if scaling is also a problem.

Industrial low-pressure boilers, particularly if they are of the steam generating type, rather than hot-water boilers, owing to their large make-up requirements, and also because of their mode of operation, may perform more satisfactorily with a softened water than with untreated supply. However, as many softened waters are intrinsically corrosive, some dosage to control pH and dissolved oxygen concentration will probably also be desirable (after base-exchange treatment, for example). With increasing boiler pressure, the use of treated water and supplementary dosage become increasingly desirable, as the carry-over of boiler-water solutes in steam becomes more pronounced, and the plant is less tolerant of scaling. A high degree of purity is therefore essential for the feed-water to lessen the risks of carry-over and scaling and to provide a basis for effective anti-corrosion measures.

Deposit formation, due either to 'crud' (suspended matter—mostly metallic oxides) transported into the boiler or to the products of corrosion in situ, is undesirable as, in many parts of the system, quite apart from the risk of overheating which they present, deposits are able to participate in a mechanism for concentrating solutes to unacceptably high corrosive levels, and are particularly dangerous in high-pressure plant (see Section 4.5).

It is particularly important to avoid waters which are inherently acidic or those which might become so in operation, e.g. those containing the chlorides of magnesium or, to a lesser extent, calcium, which undergo hydrolysis at elevated temperatures. This can be done either by removing such salts externally in a softener or by dosing enough alkali into the system to neutralise the acidity produced.

Boiler Corrosion: Low-Pressure Plant

The primary reaction in the corrosion of boiler steel is the formation of ferrous hydroxide and its subsequent decomposition to magnetite and hydrogen – the Schikorr reaction (Section 4.4). This is demonstrated by the products of corrosion encountered throughout the whole range of boiler operating pressures, but the details are influenced by other factors, i.e. the water quality, heat flux, and the boiler operating conditions.

Thus, in domestic central heating systems, the three main causes of trouble are: blockages, hydrogen generation, and the pitting of radiators. Reaction in the radiators leads to the accumulation of deposits of iron oxide which may lead to partial blockages with some parts of the circuit becoming cool, and sometimes to complete blockage, with the resultant choking of the circulation pump. Hydrogen produced by the Schikorr reaction tends to accumulate at the tops of the radiators, which then require 'bleeding' to restore circulation.

Deposits of magnetite result in the attack being concentrated beneath them (occluded cell) with increased risk of local failure. Studies by Smith¹⁷ show that 'chimneys' of magnetite tend to grow in flowing conditions on grey cast iron at 50°C in water containing oxygen.

Overheating leads to failure. This can result from scaling*, and the consequential impedance to heat transfer. A mild-steel tube, for example, which at 448°C will last for 30 years will, at 624°C, fail by creep in 9 h (see Table 17.5). Depending upon the rate of scale build-up, and the resulting rise in temperature, some associated corrosion, due to salt concentration, may also occur. Qualitatively, the control of scale in boilers is achieved by additions of sodium carbonate or phosphate. These precipitate the calcium as the carbonate or hydroxyapatite, respectively (the latter being the equilibrium form of calcium phosphate at boiler pH values). The aim is to add sufficient excess of the conditioning chemical to cause precipitation in the bulk of the solution, otherwise, nucleation may occur on the heat transfer surfaces and cause scaling. Hamer *et al.*¹⁹ suggest that the less soluble reaction products are more likely to produce the desired effect. Thus, in relatively untreated waters, calcium sulphate, which is fairly soluble, tends to form scale. The carbonate of calcium is less soluble than the sulphate, and hydroxyapatite still less so. This would account for phosphate conditioning tending to form a 'sludge', i.e. a precipitate, in the bulk solution, rather than the scale, which is often associated with inadequate carbonate dosage.

In addition to carbonates and/or phosphates, a variety of substances have also been used to act as 'sludge conditioners'—e.g. starches, lignins, polyacrylates etc. Other substances, such as nitrites and sulphates are claimed to have some value in the suppression of caustic cracking (see Section 5.1).

Apart from caustic cracking, the main forms of corrosion in low-pressure plant are oxygen pitting and scab formation. The residence of oxygen at sensitive locations on-load, possibly following off-load initiation, means that

*Although the presence of oil in the boiler water, or water starvation may also cause overheating.

Table 17.5 Creep lives of mild steel tubes at various temperatures (By permission of M.T. Robinson)

Time to rupture	Temperature (°C)					
	Minimum		Mean		Maximum	
	C-Mn Steel	Mild steel	C-Mn Steel	Mild steel	C-Mn Steel	Mild steel
9 h	624	615	650	640	677	664
24 h	607	599	631	622	658	645
5 days	579	571	602	593	626	614
10 days	567	560	589	581	612	601
100 days	527	521	546	539	567	557
(2 400 h)						
3 years	488	482	504	498	522	513
(24 000 h)						
30 years	448	443	461	456	476	469
(240 000 h)						

the cathodic half-cell reaction is available to complete the corrosion mechanism. The scab type of corrosion may develop at sites of initial oxygen pitting or in the vicinity of scale or other deposits. Its severity arises from the occluded nature and hence the increased concentration of the corrodant, which may be due to excursions in the boiler water chemistry. The presence of the deposit restricts diffusion away from the corroding site, so that corrosion propagates, and further deposits accumulate, thus aggravating the situation. Reaction is accelerated by temperature and heat flux, and, in sensitive areas, final failure may be by corrosion or by overheating.

As has been noted, scaling due to inadequate water treatment may, in the short term, lead to efficiency losses but, eventually, could result in overheating and possibly to associated corrosion. Awareness of this has led to an increasing use of appropriate water treatment with increasing boiler pressure. Scaling due to hardness salts is therefore less common now than formerly, but deposits caused by other means may occur with similarly undesirable consequences.

Boiler Corrosion, High-Pressure Plant

In high-pressure boilers, there are three types of on-load corrosion: acidic chloride, neutral chloride/dissolved oxygen, and caustic attack. The first and second (once it becomes established) are brittle and thick-walled and are accompanied by hydrogen damage which can lead to failure within a few hundred hours. Caustic attack tends to produce a 'gouged' appearance of the metal due to extensive wastage. The morphology is fairly characteristic of the failure type. Acidic chloride forms hard, laminated oxide, whilst, with caustic attack, the oxide is often soft, and, as it is easily removed, may be absent.

The rate of corrosion in any of these three modes is substantially higher than in normal circumstances. In the absence of off-load corrosion, rates of accumulation of magnetite on boiler tubes range from 1 to 2 $\mu\text{m}/1\,000\text{ h}$. In contrast, on-load corrosion rates are from 20 to 1 000 times these values. The oxide forms as a duplex layer, although both layers are not invariably present. In waterside deposits, the outer layer, nominally of magnetite, also

contains the oxides of, for example, copper and nickel, which derive from the metals of construction of the feed system, as well as traces of silica, **calcium** etc. which originate in the raw water and 'slip' through even high-performance water treatment plants. Acid chloride failures on plant are usually caused by ingress of cooling water into the feed-water. In the boiler, constituents of the cooling water, mainly calcium and magnesium salts may suffer hydrolysis to acidic products, given an appropriate water chemistry. Neutral chloride type corrosion occurs owing to the production of an acidic environment in occluded sites to complement the cathodic reduction of dissolved oxygen at the surface, e.g. around a pit. Caustic attack usually arises, not from contaminant ingress, but from excursions from target values of conditioning chemicals.

All of these types of corrosion may be produced in the laboratory, but only at concentrations far greater than those employed on plant, showing that concentration mechanisms are operative in the real situation.

Corrosion Control

Corrosion Control in Low-Pressure Boilers

In some cases, given a benign water supply and a system free from leaks (which if present would lead to high make-up requirements and a correspondingly high rate of oxygen ingress), untreated mains water is adequate for domestic central heating boilers. Where these conditions do not apply, then some conditioning of the feed-water is advisable.

Whilst a number of failures in low-pressure plant are due to overheating, rather than corrosion, these should be avoided by suitable water treatment, conditioning and operation. As regards corrosion, deaeration is an effective counter-measure to oxygen pitting. Scab formation could arise from the presence of deposits or from the effects of excessive concentrations of chemicals (the former may well lead to the latter). Anti-scaling measures, together with effective control of dissolved oxygen (as discussed in Section 4.2) should largely eliminate deposits. The control of chemical conditions should be implemented according to the recommendations of BS 2486 and to the specific type and pressure class of the boiler.

For the particular problem of caustic cracking remedial measures include¹⁹:

1. Restraining the sodium hydroxide concentration held in the bulk boiler water.
2. Adding other substances which are claimed to act as palliatives for this form of attack. These include: sodium sulphate, sodium nitrate and certain tannins. Experience indicates that the maintenance of certain ratios of chemicals is helpful to vulnerable boilers, e.g. sodium sulphate to sodium hydroxide a ratio of 2.50, and sodium nitrate to total alkalinity of 0.4.

Corrosion Control in High-Pressure Boilers

With high-pressure boilers operating above about 60 bar, the complete removal of hardness salts from the feed-water by one means or another is

highly advisable if inconvenience is to be avoided. This means that one form of scaling is therefore preempted. However, deposits due to the products of corrosion of the boiler or the feed system, subsequently transported into the boiler, are still possible and these may well lead to overheating and associated corrosion.

As the extent of solute concentration depends (amongst other factors) upon the thickness of the deposit, then clearly the degree of concentration can be limited by chemical cleaning at intervals (see Section 5.6). In addition, the strength and corrosivity of the solutions developed is influenced both by the nature and the amount of the chemicals present. Thus, when sodium hydroxide is used as an alkalising agent, the aim is to achieve in the boiler a NaOH:NaCl ratio of 1:1 on a molar basis (equivalent to 1:1.5 on a weight basis). This, in turn, is linked to an upper limit on the chloride determined by the boiler operating pressure to minimise carry-over. Amines are the main alternative alkalising agents to the solid alkalis. Their weak basicity precludes the development of unduly high alkalinities. In addition, there is limited scope for increasing the concentration of amines to raise the pH of the boiler water as, owing to their fairly high volatility, they are carried over in steam and high concentrations would present a threat to the copper alloys in the condenser and feed system.

A serious disadvantage of volatile alkalis becomes apparent when acidic conditions arise in the boiler due, for example, to cooling water ingress from leaks in the condenser. In the concentration situation at the boiler-tube surface which precedes severe corrosion, whilst the salt concentration increases to the extent determined by the concentration factor, the amine is prevented from matching this by its volatility. In addition to this loss of material into the steam phase, the amines are too weakly basic to be capable of effectively neutralising strong acids. In such circumstances, then, if the ingress of contaminant cannot be stopped, the type of conditioning should be changed from volatile to solid alkali. If, however, the design of the plant is such that only volatile alkalis are permitted for conditioning, then condensate polishing emerges as the only option if the plant is not to be taken off load every time contamination occurs.

The third main type of alkalising agent is the alkali phosphate. Sodium mono-, di- and triphosphates in appropriate proportions may be used to achieve the desired conditions. In addition to their use to prevent scale phosphates have the advantage for corrosion control of being pH buffers so that they limit the attainable concentration of free hydroxide ion in solution and so restrain the scope for corrosion of the caustic type.

This behaviour has been harnessed in certain specific modes of boiler-water control. Coordinated conditioning aims at maintaining essentially Na_3PO_4 , i.e. a Na: PO_4 ratio of 3:1. The concentration should be within the range 5–30 mg/kg PO_4 , the actual value decreasing with increasing boiler pressure. In this way, ingress of acidic material is coped with as hydroxide is produced by ionisation to exactly match it, but at the same time excess alkalinity, and so the risk of caustic attack, is less likely.

It is found, however, that in sensitive situations this mode of conditioning may still lead to undesirably high amounts of acidity or alkalinity. This is caused by the precipitation from solutions of tri-sodium phosphate of material with an excess of sodium so that the residual solute is

correspondingly depleted. This can be avoided by working at a Na:PO₄ ratio of about 2.7:1 – termed ‘congruent’ phosphate. Concentrations of up to 20 mg/kg PO₄ are maintained with this regime, depending upon boiler pressure.

For both coordinated and congruent control, the pH depends upon the phosphate concentration and the sodium to phosphate ratio. Generally, however, phosphates are unsuitable for use at boiler pressures above 100 bar as their low solubility and high concentration factors developed lead to corrosive conditions.

Once-Through Boilers

Engineering considerations in some cases dictate that boilers should be of the once-through design rather than of the drum type, for both fossil- and nuclear-fuelled plant. For instance, the once-through design needs fewer penetrations of the pressure shell in its construction. It may be noted that the once-through type has been rendered practicable only by the availability of high purity water. In once-through boilers the water is converted into steam progressively in a process of continuous transition through the plant, each tube functioning along its length in turn as economiser, evaporator, superheater etc. There is thus no real distinction between feed and boiler water. There are no facilities for blowdown, and solutes entering the boiler must either be deposited, or leave with the steam (unless they undergo chemical change).

Once-through boilers may be either sub- or super-critical. Sub-critical boilers are clearly at some potential risk of on-load corrosion owing to the presence of the evaporator zone. Measures aimed at avoiding on-load corrosion include – keeping the overall solute concentration low, keeping the ionic balance matched, and maintaining the waterside oxide suitably thin. With super-critical plant, there is no chance of on-load corrosion whilst it is operating in the super-critical mode, as there is no phase boundary. The risk is present, however, when the plant is run in the sub-critical mode, as all super-critical plant must be at times.

As for the turbines, no steam-purifying equipment of the type used on drum boilers is feasible, so that the steam from super-critical boilers tends to be of inferior quality. Deposits have been reported of cuprous oxide on the extra high-pressure turbines and of cupric oxide on some high-pressure turbines of sub-critical plant. These deposits may lead to a loss of efficiency and to some risk of corrosion. At intervals, slugs of solute are carried over in the steam, which is therefore of fluctuating quality. This is countered by periodic water-washing of the boilers.

Overall, these features mean that chemical control standards are necessarily high. For example, supplementation of the water treatment plant by condensate polishing plant and periodic chemical cleaning are particularly important. In addition, before each period of operation, a clean-up of the cycle is applied to remove crud. Stringent attention must be paid to the feed-water conditioning.

As an example of a standard for feed-water for a once-through boiler BS 2486 gives a maximum conductivity of 0.2 μ S/cm at 25°C and pH in the

range 8.5–9.2 or 9.2–9.5, depending upon whether or not copper alloys are present, with the following maximum quantities of impurities 50 µg/kg total solids, 5 µg/kg dissolved oxygen, 20 µg/kg silica, 19 µg/kg iron and 2 µg/kg copper nickel 2 µg/kg.

Nuclear Plant

It is not the intention here to consider in detail the subject of boiler feed-water conditioning and treatment for nuclear plant, but the general principles may be noted. Essentially, the same objectives apply as in fossil-fuelled plant, embodied in the three aims to minimise corrosion, deposition and steam-carryover. Requirements are more stringent in nuclear plant because there is no possibility of repairing tubes which have failed, let alone those which have suffered either deposition or corrosion. Again, certain tubes in nuclear plant have very modest design corrosion allowances so that only minimal loss of thickness from any cause can be tolerated.

The objectives are sought by much the same means as in conventional plant, although with higher standards of purity for any given pressure class. Thus, with deaerated feed-water, dosed with hydrazine and ammonia, sodium hydroxide and/or alkaline phosphate or 'all volatile treatment' are widely employed. In other cases, virtually the same principles apply, but with different reagents, e.g. alkaline borate (cf. alkaline phosphate) has been used. In nuclear practice, condensate polishing tends to be more commonly used than on fossil-fired plant. Water purity tends to be higher and the types of boiler and feed-water conditioning tend to be more sophisticated with increasing complexity of the plant.

Boiler and Feed-Water Standards

A number of authorities have issued standards for boiler and feed-water. These include boiler manufacturers, water treatment firms and the British Standards Institution, as well as other interested bodies. The authorities noted here to illustrate the scope for similarities and differences in this field are as follows: Central Electricity Generating Board (CEGB)³, Electric Power Research Institute (EPRI), as discussed by Smock²⁰, British Standards Institution (BSI) 'Treatment of Water for Land Boilers' (BS 2486:1978), American Society of Mechanical Engineers (ASME), as discussed by Simon and Fynsk²¹ and the (VGB) Guidelines as noted by Smock²⁰ and by Bolton and Ray²². All of these authorities emphasise that their standards are essentially guidelines and advise that in any given case the views of the boiler manufacturer should be sought and local circumstances taken into account.

Certain general points emerge from these guidelines:

1. Softened water is recommended for boilers in the range 13–40 bar.
2. Demineralised water is recommended for boilers in the range 40–60 bar.
3. Increasingly pure demineralised water is recommended for those boilers operating above 60 bar.

The different specifications recognise the need to deal simultaneously with the three main aims of treating and conditioning of boiler water, i.e. to minimise corrosion, deposition and carryover. Thus, the increasing stringency of the water treatment, as indicated above, takes account of the need to diminish scaling. At the same time, the progressive increase in total dissolved solids content which this trend to higher purity water brings about also tends to compensate for the increased tendency to carryover with increasing pressure. In addition, between these last two requirements, which produce waters too soft to scale and too dilute to lead to significant carryover, is a range of waters which, in each specific case, have to be conditioned to restrain corrosion.

The boiler-water standards for shell boilers, as given in BS2486:1978 for 2, 20 and 40 bar, respectively, indicate that some parameters are fairly insensitive to pressure, whilst others are not. Thus, sodium phosphate should fall within the range 50 to 100 mg/kg and sodium sulphite between 30 and 70 mg/kg for each of these pressures. Total alkalinity should have a maximum value of 1 200 mg/kg at 2 bar and 700 mg/kg at both 20 and 40 bar, with the corresponding caustic alkalinity at 350 300 and 200 mg/kg. Silica should be less than 40% of the caustic alkalinity in each case. Total hardness should be undetectable in all cases. Dissolved solids maxima are given as 3 500, 3 000 and 2 000 mg/kg, again at 2, 20 and 40 bar.

The inverse relationship between dissolved solids concentration and pressure is illustrated by the figures given for low-pressure boiler waters in Table 17.6. That there is room for different opinions is shown by contrasting the BSS and ASME recommendations. Whilst both of these authorities propose essentially similar figures for feed-water (Table 17.7), some of the ASME boiler-water figures are substantially below their BS equivalents. This is probably due to the increasing trend towards higher heat fluxes than formerly in some low-pressure plant, particularly waste-heat boilers.

Table 17.6 Feed-water standards for low- to intermediate-pressure boilers

	Issuing authority					
	BSS	ASMF	BSS	ASMF	BSS	ASME
Pressure (bar)	20	20	40	40	60	60
pH at 25°C	8.5/9.5	7.5/10.0	8.5/9.5	7.5/10.0	8.5/9.5	7.5/10.0
Total hardness (mg/kg)	10	0.3	2	0.2	0.5	0.1
SiO ₂ (mg/kg)	Note 3	<0.05	Note 3	<0.02	Note 3	<0.01
Total iron as Fe (mg/kg)	NA	<0.10	NA	<0.03	0.02 ^a	<0.02
Total copper as Cu (mg/kg)	NA	<0.05	NA	<0.02		<0.015
Oil (mg/kg)	ND	<1	ND	<0.5	ND	<0.5
Total organic carbon (mg/kg)	Note 4	<1	Note 4	<0.5	Note 4	<0.5

In this Table, BSS refers to British Standard Specification 2468: 1978, and ASME refers to the American Society of Mechanical Engineers Industrial Boiler Sub-Committee of the Research Committee on water in Thermal power stations, 1986

NA, not applicable; ND, not detectable

^aSum of iron, copper and nickel.

Note 1: Shell boiler feedwater specifications are usually limited to pH alone.

Note 2: pH and ammonia limits depend on whether or not copper-based alloys as well as ferrous materials are present in the feed system.

Note 3: The concentration should be such as not to require blowdown of boiler water in quantities exceeding either the design value or feedpump capacity.

Note 4: Total organic carbon is not specified but it is stated that values for organic matter depend on circumstances.

Table 17.7 Water tube boilers – examples of low-pressure boiler water standards

Parameter	Pressure, bar							
	20		40		60		100	
	BSS	ASME	BSS	ASME	BSS	ASME	BSS	ASME
SiO ₂ mg/kg	0.4 CA	150	0.4 CA	40		20		2
Total alkalinity as CuCO ₃ mg/kg	700	350	500	250	200	150	100	NS
Free hydroxide as CuCO ₃ mg/kg	300	NS	150	NS	30	NS	10	ND
Electrical conductivity μ S/cm@25°C		3500		2500		1500		150
Total dissolved solids mg/kg	3000		2000		1200		350	

In this Table, BSS refers to British Standard Specification 2468: 1978, and ASME refers to the American Society of Mechanical Engineers Industrial Boiler Sub-Committee of the Research Committee on water in Thermal power stations, 1986
 ND, not detectable NS, not specified.

Table 17.8 Feed-water standards for high-pressure boilers

	Issuing authority ^a					
	CEGB	VGB ^b	BSS	BSS	ASME	ASME
Boiler pressure (bar)	100/165		100	130	100	130
Elect. Conductivity μ S/cm 25 degC		0.3				
pH at 25°C	8.8/9.3 ^c			8.5/9.5		9/9.6
Dissolved oxygen (μ g/kg)	15 (EP) ^d 5 (EF)	20		5		7
Iron as Fe (μ g/kg)	10 ^e	30	10 ^e			10
Copper as Cu (μ g/kg)		5				10
Silica as SiO ₂ (μ g/kg)		20				
Oil (μ g/kg)	< 100	< 500				< 200

^a The full titles of the authorities issuing these standards are given in the text.

^b VGB standard also includes upper limits of 1ug/kg for carbon dioxide and 5ug/kg for chemical oxygen demand.

^c Secondary parameter.

^d 'EP' and 'EI' denote 'extraction pump' and 'economiser inlet', respectively.

^e Iron plus copper plus nickel.

At boiler pressures above about 85 bar, the tolerable level of total dissolved solids is so low that all the parameters specified are necessarily low in value. Several examples of recent specifications are given in Table 17.8 (feed) and 17.9 (boiler).

Implementation of these standards depends upon a number of factors:

1. Solid alkalis may hide-out in some boilers so that the operator has little choice but to apply 'all volatile treatment' (AVT)
2. Phosphate, if it does not hide out, may be difficult to control as the ratio Na:PO₄ is affected by substances other than those added for alkalisation.
3. Whilst AVT cannot itself cause on-load corrosion, it provides only limited protection against acidic contamination.
4. In addition to the chemical requirements, a number of other factors affect the susceptibility of the system to on-load corrosion, particularly operation and design.

Table 17.9 Boiler-water standards for high-pressure boilers

	Issuing authority ^a									
	ASME		VGB		CEGB ^e			EPRI ^b		BS 2486
	Consensus				Solid alkali		AVT	With reheat	Without reheat	
Pressure (bar)	100	133	60	160	100	165	100/165	60–200	60–200	60–80
Electrical conductivity at 25°C (μS/cm)	<150	<100	<2 500	<50						
pH at 25°C			9–10.5 ^f		Not a primary standard			9.1–10.2 ^d	9.1–10.2 ^d	
Caustic alkalinity as NaOH (mg/kg)	Not detectable				1.5 × NaCl					24
Silica as SiO ₂ (mg/kg)	<2	<1	0.25–8 ^f		<2	<0.2	<2–<0.2	0.1–3.5	0.2–7	20
Chloride as Cl (mg/kg)					<4	<2	0.2 (NaCl)	0.5–4	1–8	
Phosphate as PO ₄ (mg/kg)			<6					<10 ^c	<20 ^c	12
Sulphate as SO ₄ (mg/kg)								1.5–4.5	3–9	30
Total dissolved solids (mg/kg)										<1 200
										350

^a Authorities names given in full in the text. ^b EPRI values depend on pressure. ^c Depends on pH and sodium to phosphate ratio. ^d Depends on PO₄ and ammonia. ^e CEGB also specified a minimum NaOH. ^f Depending on pressure.

Variable-load operation may result in higher heat fluxes than on base-load, as well as unusual chemical conditions. If, however, after allowing for these, and remedying them as far as is practicable, a boiler persistently suffers from on-load corrosion, then the cure may lie in a design change.

As regards steam purity, standards have not usually specified more than a few parameters. Thus, both CEGB and VGB put upper limits for sodium and silica of 10 and 20 $\mu\text{g}/\text{kg}$, respectively. In addition, VGB specify upper limits or conductivity of 0.3 $\mu\text{S}/\text{cm}$ at 25°C, for iron of 20 $\mu\text{g}/\text{kg}$ and for copper of 3 $\mu\text{g}/\text{kg}$. There are indications that fuller specifications may be introduced for steam standards. EPRI's Consensus Guidelines suggest upper limits for sodium (5 $\mu\text{g}/\text{kg}$), chloride (3 $\mu\text{g}/\text{kg}$), sulphate (3 $\mu\text{g}/\text{kg}$) and silica (10 $\mu\text{g}/\text{kg}$) for drum boilers on phosphate treatment, and with reheat. For plant without reheat, the values are doubled. For drum boilers on AVT, the sodium level is slightly modified to 3 and 6 $\mu\text{g}/\text{kg}$ for plant with and without reheat, respectively, chloride, sulphate and silica remaining unaltered. A common value of 100 $\mu\text{g}/\text{kg}$ is proposed for 'total organic carbon'. Conductivity is given as 0.3 and 0.35 $\mu\text{S}/\text{cm}$ for drum boilers with and without reheat on phosphate treatment.

The implementation of feed- and boiler-water and steam standards should be linked to an appropriate scheme for sampling and analysis. Departures from target conditions should be responded to by instituting appropriate remedial measures and increasing monitoring until conditions are restored to normality. Some authorities assess the permissible degree of contamination on a cumulative basis, i.e. using a factor derived from the product of concentration and time in any given operational period.

Chemical Cleaning

At times it may be desirable to chemically clean various parts of the boiler plant and its auxiliaries. The reason may be curative or preventative. With low-pressure boilers and heat-exchange equipment, cleaning is carried out to restore heat transfer, and, for boilers, to prevent overheating. With higher pressure boilers, the restoration of heat transfer is trivial and, whilst some overheating may be avoided, the main reason for chemical cleaning is to prevent corrosion. In nuclear plant, an additional reason for cleaning is to remove radioactive material and improve safety.

With heat exchangers, cleaning should be considered as an option when the efficiency has fallen off to some specific level e.g. a terminal temperature difference. With boilers, unless there has been some occurrence which may be alleviated by a particular clean, periodic cleaning to pre-empt corrosion by limiting deposit thickness should be considered²³.

Cleaning is usually carried out in several successive stages on the off-load plant e.g. flushing (to remove easily detached debris), degreasing (both to remove organic material and to permit easier access of the cleaning reagents to the metal surface), dissolution of hardness scale and/or metallic oxides (both grown and deposited), neutralisation, and, if necessary, passivation. Intermediate rinse stages also feature in the sequence. There may also be the need for ancillary stages such as, in boiler cleaning, copper removal.

Degreasing is usually undertaken by means of alkaline and/or organic reagents. The dissolution of hardness scale and oxides is carried out with

acids and/or complexants. This requires the presence of an inhibitor to restrain attack on the substrate metal after descaling. Typical cleaning solutions are hydrochloric acid, citric acid (used in the form of the monoammonium salt), hydrofluoric acid, sodium or ammonium EDTA and, for certain specialised applications, LOMI (low oxidation-state metal ions) reagents²⁴. Passivating formulations may be any of a variety of alkalis, sometimes used in conjunction with oxygen scavengers.

Chemical monitoring is employed to follow the course of the clean and to identify the end of each stage.

Boilers and certain new process plant may be subjected to a steam blow after chemically cleaning, but before commissioning.

Operational and Design Factors

Operational and design factors also influence on-load corrosion. Thus, as was noted in Section 4.5, the bulk boiler-water concentrations of a number of solutes can be transformed into those strengths which are capable of causing on-load corrosion. Heat flux influences the degree of concentration developed and this, in turn, may be affected by fluid flow, and by oxide thickness. Some operational factors may differ during variable load operation (e.g. two-shifting) from their value on base-load, as indeed may the boiler-water chemistry. Corrosion fatigue may occur²⁵. The role of hydrodynamic parameters has been discussed by a number of workers. Gardner draws attention to the possible influence on on-load corrosion of: tube-inclination, surface condition, poor circulation, temperature elevation, sub-cooling, partial and final dry-out, particulate deposition, and parallel channel stability²⁶. Klein considers temperature elevation for three conditions of boiling and relates this to overheating failures²⁷. Low angle tubes, he suggests, are more susceptible to on-load corrosion owing more to preferential deposit accumulation than to heat adsorption. Klein also mentions weld backing-rings and tube (bore) mismatch as factors in deposition. It must be noted that heat fluxes can vary widely in boilers²⁸. The trend to higher heat fluxes recently in lower pressure plant means, in effect, that standards of boiler-water quality need to be enhanced, conditions for a higher pressure boiler being adopted for a lower²⁹.

Steam Purity

Steam needs to be of an acceptable degree of purity for any given plant because:

1. Deposition and corrosion can cause loss of turbine efficiency.
2. Material deposited on-load may, when conditions become wet in the off-load plant, cause corrosion.
3. If the steam is used in certain manufacturing processes, contamination may be undesirable, e.g. in food plant.

Solutes are carried over in steam in two ways – mechanical and chemical. Attempts are made to control mechanical carryover by steam washing, e.g. cyclones and chevron washers etc. Mechanical carryover increases with

pressure, and at 160 bar is about 0.1%. Chemical carryover occurs because of the intrinsic solubility in steam of solutes³⁰, boiler operating pressure determining the degree of partition between steam and water. The most commonly experienced problems with steam solubility occur with silica, and boilers, when necessary, are run at reduced pressure to minimise carryover of silica and its subsequent deposition on turbine blades, which would lead to a consequent loss of efficiency. Silica is soluble in steam under the conditions obtaining in the low pressure turbine to the extent of about 0.02 mg/kg. For boilers operating at 65, 100 and 165 bar, the permissible boiler water concentrations of silica to avoid carryover are about 20, 2 and 0.2 mg/kg, respectively. Some other solutes exhibit a greater dependency on pressure than silica so that trouble may be experienced at, for example, 165 bar, but not at lower pressures. This is found with copper oxide in some (but not all) supercritical turbines, and even in some subcritical high-pressure turbines. Again, sodium sulphate is deposited in the primary reheaters of some 165 bar boilers, but rarely to any extent in those in lower pressure plant.

In general, the concentration of any impurity in steam should not exceed the amount present at the location of minimum solubility in the circuit³¹.

Corrosion in the Steam/Water Circuit Due to Solute Carryover

There is extensive literature dealing with the consequential corrosion in steam/water circuits after solute carryover. It is not the intention to discuss it here at any great length, but two examples are given to illustrate some aspects of the subject.

Superheaters Service conditions often dictate the choice of austenitic materials for part (the secondary stage) of the superheater. These materials are susceptible to stress-corrosion cracking, the principal corrodants being chloride and caustic alkali. As these feature in many boiler-water chemistry regimes, there is clearly a need to minimise their entry into the superheater. On-load, sodium concentrations in steam are limited to less than 0.005 mg/kg Na (twice this for ferritic superheaters). Before service, care should be taken to prevent the ingress of adventitious impurities, either solid, e.g. pulverised fuel ash, or in solution. Thus, in chemical cleaning, for example, 'low chloride' citric acid should be used and demineralised water used both for making up the solution and for any flushing, rinsing, etc.

Reheater Corrosion In certain large steam generating units, a reheat stage is included in the cycle. Briefly, steam from the boiler is first passed through the superheaters and then through the high-pressure turbine. It is then taken through the reheaters before being passed through the intermediate-pressure and low-pressure turbines. If any solids are carried over in the steam, their solubility is determined by the temperature and pressure, and a point of low solubility in the cycle is the primary reheater. Any material so deposited presents no problem during operation, as dry conditions prevail. However, off-load, condensation may occur and lead to the formation of corrosive solutions from the deposited material. Sodium sulphate is the substance most prone to deposition in reheaters, although in some cases this may be accompanied by sodium hydroxide. The form of reheater corrosion is different for ferritic and austenitic steels.

In ferritic steels, typically in this context, 1% or 2% chromium-

molybdenum, the corrosion occurs as saucer-shaped pits, at rates up to $2\text{ mm}/10^4$ off-load hours. In austenitic steels, the corrosion is intergranular, with similar rates.

Remedial measures include: stringent attention to chemical control, drying, and/or nitrogen blanketing of the reheater during off-load periods, periodic water-washing to remove the deposits (although unless the plant is thoroughly dried out afterwards this may lead to enhanced corrosion) and, possibly, if necessary, changing the material of construction of the primary reheater.

Off-Load Protection

General

Protection from corrosion during off-load periods is an essential supplement to on-load control measures. Such corrosion may assume a number of forms. Off-load corrosion, e.g. rusting, may occur at rates of up to 1.5 mm/year and may take place under atmospheric or immersed conditions. Sites so attacked may propagate further when the plant is on-load. When plant is taken out of service, ingress of air and water, together with acidic gases, possibly carbon dioxide and sulphur oxides, may transform a previously benign environment into one which is undesirably aggressive. Off-load corrosion may occur both before initial operation and in the intervals between periods of service.

Before Commissioning

The periods before commissioning include fabrication at works, storage, transport, perhaps storage on site, and then further storage after construction. The means of protection employed are also influenced by the nature of the plant item in question. Tubes, for example, which form the greater part of the internal surface of many industrial installations, may be chemically cleaned at works, rinsed, dried by means of warm air blowing before being treated with vapour-phase inhibitors and sealed with plastic closures — either caps or plugs. The external surfaces of tubes should also be protected. This may be done by any of a number of protective coatings available for this purpose. The protected items should then be stored under cover, away from the effects of direct weathering, and preferably on racks which themselves stand on a concrete floor.

Partly fabricated components, e.g. feedheaters, may be cleaned at works and then 'cocooned' in the presence of vapour-phase inhibitors or desiccant until they are welded into the system. The inhibitors are usually a mixture of two substances, one with a high volatility, the other with a low volatility, e.g. cyclohexylamine carbonate and dicyclohexylamine nitrite, to provide more effective all-round protection in varying seasonal and diurnal conditions. A high degree of dryness is essential for an acceptable standard of performance of vapour-phase inhibitors. Boiler drums may be partly cleaned at works but, in many cases, still require some further degree of cleaning before commissioning, e.g. prior mechanical cleaning followed by chemical cleaning on site when construction is complete.

Condensers and turbines are not generally cleaned on-site in the same way as boilers etc. but may require treatment to remove the protective coating employed between fabrication and commissioning. These coatings are classified as 'removable' or 'non-removable' depending upon whether a specific removable stage is necessary or whether the coating can be left to wear off during operation. Turbine lubricating systems receive particular attention, being invariably subjected to a flush with oil and, if necessary, chemically cleaned.

The condition of stored plant should be monitored and, if and when necessary, the protective measures reinstated after any cleaning which may be required. If the degree of deterioration in storage of any component exceeds certain criteria, that component should be rejected.

After Service

After service, either wet or dry methods may be used for storage³². The period of storage is fixed by operational or maintenance requirements. For example, if a boiler is likely to be required for service at a few hours notice, then it can neither be drained nor dosed with any substance which is incompatible with its operational chemistry. Short-term storage of up to, say, three days, may be achieved by 'nitrogen capping' over the boiler water. Longer term storage may be started by blowing the boiler empty at a pressure of a few bars so that, at least initially, the relative humidity is too low for corrosion to occur. However, in time (days or weeks depending upon the prevailing conditions) the humidity will increase so that additional protective measures will be necessary. Long-term wet storage is sometimes employed. For this purpose, alkaline solutions, in some cases with added oxygen scavengers are used.

For high-pressure plant, volatile reagents are preferred even for storage in case any chemical is inadvertently left in during subsequent operation. As with on-load protection, ammonia and hydrazine are used. With ammonia alone, a pH value of greater than about 10.5 is desirable, whilst with ammonia and hydrazine together, about 50 mg/kg of each, giving a pH value of about 10.0, is adequate.

Mixtures of sodium borate and nitrite have been used to store plant. The solution may either be left in. If this is impracticable, for instance if the plant needs to be drained for maintenance purposes, then the solution may be drained from the plant after initial dosing so as to leave locations which are difficult to drain containing a residue of inhibitive solution³³.

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18 NON-METALLIC MATERIALS

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18.1 Carbon

Carbon is a relatively inert element chemically and is used in its graphitic and pre-graphitic forms as a construction material under a variety of corrosive conditions. Modern uses include heat exchangers in chemical plants, consumable electrodes in a variety of metallurgical processes and the components of rocket motors and the moderators of gas- and liquid-cooled nuclear reactors. The demand for carbon products at the present time is $\sim 10^6$ t/year.

Manufacturing Processes

The majority of carbons produced for commercial use, that is as electrodes and nuclear graphite, are produced from cokes, coals or existing natural or synthetic graphite as follows:

1. The carbon raw material in the form of coke, coal or natural or synthetic graphite is ground and sieved (following calcination at 700–1300°C to control volatiles, if necessary) to give a desired particle size distribution. The distribution depends upon the size of the artifact to be formed and the method of forming.
2. The graded material is mixed with a pitch binder to produce mouldable body.
3. The mix is formed by extrusion, moulding or hydrostatic pressing into a 'green' artifact.
4. The artifact is then baked in a bed of granular coke to give protection from oxidation in order to drive off volatile matter and carburise the pitch binder to give a rigid body. The baking temperature is generally 750–900°C and the heating cycle time some tens of days. At this stage the material is neither amorphous nor crystalline and may be termed meso-morphous.
5. The material density, strength etc. may be improved by further cycles of pitch impregnation and baking, the effect of each successive cycle tending to be smaller, but two such cycles are not unusual for high quality graphites.
6. The product may then be finally heat-treated in an Acheson furnace at temperatures up to 3000°C to produce 'electro-graphite' in which

the crystallite perfection approaches that of natural graphite, but the crystallites are much smaller, and the density is significantly less than the theoretical value. The properties of the material may be isotropic or not, depending upon the degree of anisotropy and anisometry of the ground-up material particles and the method of forming. Very high purities (e.g. as for nuclear graphite) may be produced by choice of raw materials or a halogen-based purification in the first heat treatment.

The product of this process can be modified in many ways. It can be made impervious by impregnation or its pores may be filled with metal such as in motor and generator brushes. It must be appreciated that by choice of raw materials and processing it is possible to produce a wide range of carbons, carbon/graphites and electro-graphites. The physical properties shown in Table 18.1 are thus to be taken only as broadly representative.

A second class of carbons important because of their corrosion resistance are the 'glassy' vitreous or polymer carbons. These carbons are produced by forming cellulose and various types of thermosetting resins, followed by hardening, mild heating and carbonisation. The most appropriate forming method for artifacts, such as crucibles or tubes, is mould forming. The carbonisation occurs in the solid phase and there is no significant crystallite growth even at graphitising temperatures (such carbons are known as 'hard' carbons). Typical properties of a glassy carbon are shown in Table 18.1. Production of this type of carbon requires moderate and carefully controlled baking rates because large volumetric contractions occur ($\sim 50\%$) and considerable volumes of volatiles are emitted.

A third class of carbon materials known as pyrolytic carbon or graphite is produced industrially by gas-phase carbonisation. This carbon is deposited on a heated substrate (usually electro-graphite) by the decomposition of hydrocarbons such as methane, benzene or acetylene. The reaction conditions determine whether deposition occurs in the substrate or from polymerisation in the gas phase (soot formation must be prevented). The structure of the product can be varied over a wide range from randomly oriented and low density to very highly oriented material of close to theoretical density. The perfection can be improved by post-deposition heat-treatment or mechanical working. The high thermal conductivity of this latter material in directions parallel to the substrate, and poor conductivity perpendicular to it, together with its high strength and corrosion resistance, has led to its use for rocket nozzles and throat and nose cones, high temperature gaskets, protective coating for conventional graphites and many more. Variants can be made using co-deposition to give alloys with outstanding oxidation resistance and other properties. Some properties of highly oriented material are given in Table 18.1.

The final important form of carbon is the carbon fibre formed from polyacrylonitrile (PAN), cellulose or pitch and which is finding increasing use in fibre-reinforced composites. The corrosion of carbon fibres in composites designed for use under high temperature conditions is currently a severe limitation on their use.

Table 18.1 Properties of typical carbon materials

Property	Form of carbon				
	Conventional electro-graphite		Glassy or hard carbon	Pyrolytic carbon	
	Carbon	Graphite		Carbon	Graphite
Density (g cm^{-3})	1.5–1.7	1.5–1.8	1.3–1.5	2.1–2.3	2.26
Thermal conductivity ($\text{W cm}^{-1} \text{K}^{-1}$)	0.04–0.1	1.0–2.0	0.04–0.1	4 ⊥ 0.02–0.04	20 ⊥ 0.05
Thermal expansion coefficient (K^{-1} , ~ 100°C)	1.5×10^{-6}	$0.4\text{--}5 \times 10^{-6}$	$2\text{--}3 \times 10^{-6}$	0 ⊥ 20×10^{-6}	-1.5×10^{-6} ⊥ 26×10^{-6}
Specific heat ($\text{J mole}^{-1} \text{K}^{-1}$)	8–10	8–10	8	8	10
Tensile strength (g mm^{-2})	0.7–1.6	0.4–1.5	4–7	10–20 ⊥ 0.5–1.0	— —
Modulus of elasticity (g mm^{-2})	$0.8\text{--}1.4 \times 10^3$	$0.4\text{--}1.2 \times 10^3$	$1.5\text{--}3 \times 10^3$	$3\text{--}4 \times 10^3$	$5\text{--}6 \times 10^3$
Hardness (Shore)	60–90	20–40	70–120	30–50 ⊥ 100	1 ⊥ 30–50
Permeability ($\text{cm}^2 \text{s}^{-1}$)	10–100	1–10	$10^{-10}\text{--}10^{-12}$	10^{-12}	10^{-12}
Electrical resistivity ($\mu\Omega \text{cm}$)	$3\text{--}5 \times 10^3$	$0.5\text{--}1.2 \times 10^3$	$3\text{--}6 \times 10^3$	~300 ⊥ $\sim 4 \times 10^5$	~50 ⊥ $\sim 10^5$
Comments	Heat treatment ≅ 1000°C	Graphitised 2600–3000°C		As deposited at ~2000°C	Graphitised 3000°C

|| denotes along basal plane; ⊥ denotes perpendicular to basal planes

Physical properties

The physical properties of a number of carbons are summarised in Table 18.1. It cannot be over-emphasised that the properties of all carbons can be varied over a wide range depending upon the manufacturing process. The pyrolytic graphite and the electro-graphites are widely selected for heat transfer under corrosive conditions because of their high thermal conductivities. The electro-graphite can be made impervious by impregnation. The hard carbons and pyrolytic carbons are impervious and corrosion resistant, and have good thermal insulating properties.

The strengths and Young's moduli of electro-graphites are unusual in that they increase with temperature to high temperatures. They may also show some irreversible expansion on first heating. The effect of oxidation in the porous graphite volume is to rapidly decrease the strength. If the electro-graphite, or other carbon, is impermeable the oxidation takes place only at the surface with a loss of section. If carbons, or partially graphitised bodies, are taken to temperatures above their final heat-treatment temperature further 'graphitisation' will occur and the properties will tend towards those for electro-graphite or for pyrolytic carbon. Provided no further graphitisation occurs, the density, porosity and expansion coefficient are insensitive to temperature. In the 'hard' carbons heat treatment has little effect on the properties, but can lead to large irreversible length changes above $\sim 1000^{\circ}\text{C}$ on first heating above that temperature.

The specific heats of carbons vary very significantly below room temperature, being higher the less-well graphitised the carbon, but the values are not significantly different above ambient temperature, varying from $0.71 \text{ J/g}^{\circ}\text{C}$ at 25°C to $2.09 \text{ J/g}^{\circ}\text{C}$ at 1830°C . The physical properties are extensively presented by Kelly¹.

Corrosion Resistance of Carbon

Carbon is generally unreactive at low temperatures, but it is readily oxidised at high temperatures by air (O_2), steam (H_2O) and carbon dioxide (CO_2). In the case of *pure* conventional graphite significant weight loss in 24 h would be expected (1) at $400\text{--}500^{\circ}\text{C}$ in air, (2) at 700°C in steam, and (3) at 900°C in carbon dioxide. However, these rates are dependent on the source of the carbon, partially due to variations in porosity (and hence surface area) and degree of graphitisation but also, to a marked degree, to the presence of catalytic impurities. The principal catalytic metals are alkali metals such as sodium or potassium, alkaline earth metals such as calcium and magnesium and more common impurities, iron, nickel, copper, vanadium, aluminium and manganese. A thorough review of catalytic reactions is given by McKee². In general, increasing the degree of graphitisation and decreasing the surface area reduce the oxidation rate. Graphites and carbons will oxidise slowly at low temperatures in the presence of ionising radiation. The deposition of 100 eV of energy in the gas phase produces up to three oxidising species which will attack the carbon if produced sufficiently close to a surface, which may be in-pore. This is important for the use of graphite in gas-

cooled reactors. Oxidation by atomic oxygen produced in the electrolysis of water using a carbon anode also occurs.

The oxidation reactions in different carbons are thus very different at low temperatures, but this is less true as the oxidation temperature increases. In porous samples the rapid reaction essentially suppresses the diffusion of gas within the pores and oxidation takes place only on the surface. The oxidation rate then becomes independent of the type of carbon and is determined by the flow of oxidising gases. This condition is reached at about 800°C in pure materials.

Carbons are very stable to conventional acids and bases, and as a result they are used as corrosion-resistant material for chemical equipment. However, oxidation will occur at room temperature in highly oxidising solutions such as highly concentrated nitric and sulphuric acid, blends of potassium dichromate and phosphoric acid, or potassium chlorate and nitric acid.

Impervious graphites, that is electro-graphites with appropriate resin impregnation, are used in cascade-, shell- and tube-type coolers, condensers, pre-heaters etc. in a wide variety of chemical plants. Similar resistance to corrosion applies to glassy carbon vessels and pyrolytic carbons and graphites. The corrosion resistance to principal chemical agents is given in Table 18.2.

Table 18.2 Corrosion resistance of impervious graphites

<i>Chemical</i>	<i>Concentration</i>	<i>Temperature</i>	<i>Corrosion resistance</i>
Hydrochloric acid	0–100%	Boiling point	Complete
Nitric acid		> 60°C	Partial (care necessary)
Hydrofluoric acid	< 60%	Boiling point	Satisfactory
Sulphuric acid			Partial
Phosphoric acid			Complete
Chromic acid	> 10%	> 90°C	Partial
Acetic acid			Complete
Oxalic acid		≤ 125°C	Complete
Caustic soda		≤ 50°C	Complete
Zinc chloride	All	Boiling point	Complete
Iron chloride	All	100°C	Complete
Sodium chloride	All	Boiling point	Complete
Sodium hypochlorate	5%	Ambient	Complete
Ammonium persulphate	All	Ambient	Complete
Copper sulphate	All	Boiling point	Complete
Chlorine	100%	170°C	Complete
Bromine	100%		Partial
Fluorine	100%		Partial
Acetone	100%	Boiling point	Complete
Ethyl alcohol	95%	Boiling point	Complete
Carbon tetrachloride	100%	Boiling point	Complete
Tetrachloroethane	100%	Boiling point	Complete
Ethylene	100%	Boiling point	Complete
Chloroform	100%	Boiling point	Complete
Kerosene	100%	Boiling point	Complete
Dowtherm	100%	170°C	Complete
Benzene	100%	Boiling point	Complete
Methyl alcohol	100%	Boiling point	Complete
Monochlorobenzene	100%	Boiling point	Complete

It is usual to protect carbon from oxidation at high temperature by the use of alternative gas atmospheres—these are generally hydrogen, nitrogen, argon or helium. The first two will react at temperatures above $\sim 1700^{\circ}\text{C}$ to form methane and cyanogen, respectively.

Carbon will react directly at high temperatures with many elements such as sulphur and iron. It also forms intercalation compounds in which a wide range of molecules enter the interlayer spacing of the graphite. This can lead to disruption of the material but also produces a whole new class of potentially useful materials.

Carbon is inactive in blood and is not rejected from the human body. It is therefore increasingly used in artificial limbs, tendons and heart valves.

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18.2 Glass and Glass-ceramics

General

One of the most important properties of commercial glasses is their great resistance to corrosion; any chemical laboratory apparatus, any window or windscreen provides an excellent illustration. Windows remain virtually unchanged for centuries, resisting the influences of atmosphere and radiation. A vast range of products may be safely stored in glass for decades at ordinary temperatures, and the fact that glass can be used with alkaline, neutral and acid environments allows the same equipment to be used for a variety of processes.

Glass is one of the engineer's most useful and versatile materials. There are many types of glass to choose from to provide a wide range of physical, mechanical, electrical and optical properties for practically every type of environmental condition. The transparency of glass facilitates inspection of process operations and minimises the risk of failure due to unsuspected corrosion, while the hardness and smoothness contribute to easy cleaning.

In recent years the development of glass-ceramics has further extended the range of glassy engineering materials. Glass-ceramics combine the formability of glasses with many of the advantageous properties of ceramics. They are finding increasing application by virtue of their strength and high chemical durability at elevated temperatures.

The principal difficulty associated with the use of glass equipment is the fact that glass will break rather than deform on severe impact; thermal toughening or ion-exchange techniques may be used to mitigate this disadvantage in some applications. Glass is also more prone than metals to damage by thermal shock, although this difficulty can be largely avoided by the use of low-expansion glass formulations. Finally, the size of glassware which can readily be fabricated is sometimes below the needs of a particular process.

Commercial Glasses

Glass Compositions

The term *glass* defines a family of materials that exhibit as wide a range of differences among themselves as exists among metals and alloys. The great

variety of physical and chemical properties available arises from the possibility of including almost all the stable oxides, sulphides, halides, etc. throughout the periodic table in different glass formulations¹. Many branches of the family, e.g. those borates, silicates and phosphates which are water soluble, are of little interest in the present context. It is, however, worth bearing in mind that glasses can be designed to combine particular physical properties with good chemical resistance.

For most of the commercial glass families, silica sand is the main ingredient. However, greater melting economy and flexibility of properties are achieved with the addition of other oxides and modifiers. Depending upon the choice of these additional constituents, glasses are classified into groups, including fused silica, soda-lime, lead, aluminosilicate, borosilicate, etc. A cross-section of commercial glass compositions is given in Table 18.3, the glasses listed being:

1. Fused silica
2. Window glass
3. Container glass
4. Fluorescent tubing
5. Neutral glass
6. Hard borosilicate
7. Lead tubing
8. TV tube and screen
9. Textile glass fibre
10. Glass wool insulation
11. Superfine glass wool

Table 18.3 Typical glass composition, %

	1	2	3	4	5	6	7	8	9	10	11
SiO ₂	100	72.7	72.8	71.4	71.5	80.3	57.2	67.5	54.2	63.6	57.1
Al ₂ O ₃		1.1	1.7	2.2	5.5	2.8	1.0	4.8	14.3	2.9	4.6
B ₂ O ₃					10.0	12.3			8.3	5.0	11.8
MgO		3.8		3.9					4.5	3.2	
CaO		8.4	10.5	4.6	0.2			0.1	17.7	7.3	0.4
BaO				0.8	3.0			12.0		2.6	
Na ₂ O		13.1	14.5	15.0	8.0	4.0	4.0	7.2	0.6	14.5	14.2
K ₂ O		0.5		1.7	1.2	0.4	8.5	6.9	0.1	0.6	0.8
ZrO ₂											3.8
TiO ₂											7.5
PbO							29.0				
Li ₂ O								0.5			
Others		0.4	0.5	0.4	0.6	0.2	0.3	0.3	0.3	0.3	0.4

Note. The designations 1-11 represent the various types of glasses listed numerically in the text above this table, and they will be referred to in this way in later tables in this section.

Fused silica is a general classification within which is a range of varieties and types with differences in purity, transmission and grade. This glass may be used up to 900°C in continuous service; it resists attack by a great many chemical reagents, rapid attack occurring only in hydrofluoric acid and concentrated alkali solutions.

The container glass is suitable for the storage of beverages, medicines, cosmetics, household products and a wide range of laboratory reagents.

The tubing glass is suitable for general laboratory use and chemical apparatus construction, though neutral or hard borosilicate are preferred for more severe conditions, these representing the most resistant glasses available in bulk form.

The neutral glasses are generally less resistant than the hard borosilicate type, but are more easily melted and shaped. They are formulated so that the pH of aqueous solutions is unaffected by contact with the glass, making it particularly suitable in pharmaceutical use for the storage of pH-sensitive drugs.

Borosilicates, in terms of different types available, are the most versatile glasses produced. In general, the borosilicates are grouped into six types, viz. low expansion, low electrical loss, sealing, ultraviolet transmitting, laboratory apparatus and optical grade glasses. The example given, i.e. hard borosilicate glasses, is used for ovenware, pipelines, sight glasses and laboratory ware, and combines low expansion and high chemical resistivity with chemical stability. They generally require high founding and fabrication temperatures compared with soft soda glasses.

Glasses for electrical and electronic components are represented by the lead tubing and cathode-ray-tube screen and cone glasses. These glasses do not operate under severe corrosion conditions, but surfaces must not leach excessive alkali under damp conditions or electrical breakdown can occur. The glass compositions are formulated to give the maximum electrical resistivity and moisture resistance compatible with other necessary properties.

Glass fibres present particular problems in corrosive environments due to their very high surface/volume ratios. Glasses for electrical insulation are formulated from alkali-free aluminoborosilicate glasses (generally known as *E*-glass) and are frequently specified as containing less than 1% alkali (Na_2O and K_2O). This type of glass is also used extensively for the reinforcement of plastics where its high resistivity to moisture attack ensures a durable product. The glass wools are used for less demanding applications and generally contain some alkali. Superfine wool contains zirconia and titania to enhance the chemical resistance while retaining the properties necessary for economic fine-fibre formation.

Physical Properties

Glass has been defined as 'an inorganic product of fusion which has cooled to a rigid condition without crystallising'. The atomic structure of glasses is more closely related to liquids than to crystals. The properties of glasses are manifestations of this structure, being governed in particular by the random liquid-like disposition of the network-forming ions (commonly Si^{4+} and B^{3+}), the presence of mobile, interstitial alkali ions and the 'single-molecule' nature of the lattice. The bonding within the atomic network is partly covalent, partly ionic; the network bonds are highly directional with a range of inter-bond angles, lengths and bond energies; the bonding electrons are restricted to particular energy levels within the bonds.

Table 18.4 Physical property data for some commercial glasses*

	<i>Units</i>	1	2	3	4	5	6	7	8	9	10	11
Density	g/cm ³	2.20	2.49	2.46	2.49	2.42	2.24	3.03	2.62	2.58	2.57	2.54
Strain point	°C	987	520	490	495	518	515	—	448	616	—	—
Annealing point	°C	1 082	545	540	524	565	565	437	470	657	—	—
Littleton softening point	°C	1 594	735	720	705	780	820	631	670	843	688	710
Resistivity	Ωm	10 ¹⁵ (20°C)	1.1 × 10 ¹³ (20°C)	—	9.6 × 10 ¹⁴ (20°C)	—	10 ¹⁵ (20°C)	3.2 × 10 ¹⁰ (150°C)	1.6 × 10 ⁶ (350°C)	6.0 × 10 ¹³ (155°C)	2 × 10 ⁻³ (953°C)	4.8 × 10 ⁻³ (862°C)
Dielectric constant	at 1 kHz	3.8	7.4	—	7.8	—	5.1	7.0	—	6.4 (50 Hz)	—	—
Tan δ	at 1 MHz	very small	0.03 (50 Hz)	—	0.008	—	0.02	0.0011	—	0.0009 (50 Hz)	—	—
Refractive index		1.48	1.52	—	1.51	1.49	1.47	1.56	1.51	1.55	—	—
Thermal conductivity	W m ⁻² K ⁻¹	1.38	1.05	1.02	1.04	1.04	1.13	0.84	1.01	0.97	—	—
Thermal expansion	× 10 ⁷ K ⁻¹	5.4	79.3	87	85.5	50	33	84	85.5	49	83	—
Specific heat	J kg ⁻¹	775	987 (200°C)	821	833	819	794	—	733 (23°C)	796 (23°C)	—	—
Young's modulus	× 10 ⁻¹⁰ Nm ⁻²	7.3	7.4	—	—	—	6.3	5.75	7.4	7.2	—	—

*Compositions are given in Table 18.3

The network-modifying ions (commonly alkali and alkaline-earth ions) are ionically bound to the network although the field strength and diameter of the alkali ions allow them some mobility.

The structural features are reflected in the characteristic properties of inorganic glasses and bring about a broad overall similarity in behaviour as summarised below. Values for the physical properties of the commercial glasses listed in Table 18.3 are given in Table 18.4.

Viscosity The random nature of the glass structure imparts a range of bond energies in the network, hence a characteristic feature of glasses is a continuous softening over a range of temperature, a continuous viscosity/temperature curve and the absence of a true melting point. For convenience in comparing the viscosity behaviour of different glasses, arbitrary temperatures at which the glass has specific viscosities are often quoted².

Softening temperature The Littleton Softening Point³ is most commonly used. At this temperature the glass has a viscosity of $10^{6.6}$ N s/m².

Transformation temperature, T_g T_g corresponds to a viscosity from 10^{12} to 10^{13} Ns/m² depending on the definition and on the method of measurement.

Annealing point and strain point An important range in practice is that from 10^{11} to $10^{13.5}$ Ns/m² known as the *annealing range*. The annealing point and the strain point are the temperatures at which the glass has a viscosity of $10^{12.4}$ Ns/m² and $10^{13.6}$ Ns/m² respectively. Within this range the glass is effectively a solid, but internal stresses can be relieved within a practical time scale. Rapid cooling of glass articles through the annealing range eventually results in permanent and sometimes catastrophic thermal stresses. However, it is possible to cool the glass relatively quickly from the lower end of the annealing range.

Glass behaves as a Newtonian liquid at temperatures well above the glass transition. It is this behaviour which prevents the necking observed during gross deformation of metals and which allows glass to be formed into such a large number of useful configurations.

Thermal shock resistance The ability of a glass article to withstand sudden changes of temperature depends primarily on its thermal expansion coefficient, its thickness and its design. For articles of identical shape a low expansion glass (such as a commercial borosilicate) will withstand appreciably greater temperature shocks than will glass of a higher expansion. Thermal shock-resistance testing is usually carried out by transferring the articles from a hot environment to a cold vessel containing water at a predetermined temperature⁴.

In general, transitions from a hot to a cold environment are more likely to produce failure than those in the opposite direction since they tend to induce tensile stresses at the surface.

Stress birefringence The presence of stress in glass articles may be monitored readily since stressed glass is birefringent. Standard methods exist for these measurements.

Thermal expansion Glasses having coefficients of linear thermal expansion

of from $0.5 \times 10^{-6}/\text{deg C}$ to over $10 \times 10^{-6}/\text{deg C}$ are available. High expansion glass compositions do not generally have long-term chemical durability however. Glass-ceramics are remarkable for the very wide range of thermal expansion coefficients which can be observed. At one extreme, materials having negative coefficients are available while for other compositions very high positive coefficients can be obtained. Between these two extremes there exist glass-ceramics having thermal expansion coefficients practically equal to zero and others whose expansion coefficients are similar to those of ordinary glasses or ceramics or to those of certain metals and alloys. This range of expansion coefficients is allied with good chemical durability.

Mechanical Properties

Characteristically, glasses are brittle solids which in practice break only under tension. The ionic and directional nature of the bonds and the identification of electrons with particular pairs of atoms preclude bond exchange. This, coupled with the random nature of the atomic lattice, i.e. the absence of close-packed planes, makes gross slip or plastic flow impossible.

Strength If flaws and stress concentrators, which emphasise the brittle nature of glass, can be avoided, then a glass article behaves as a single molecule in which the strength is governed by the very high interatomic bond strength. Glasses are therefore inherently very strong materials, theoretically capable of exhibiting a tensile strength of about 7 GNm^{-2} . In practice however, surface flaws act as stress concentrators under tensile loading and commercial glasses in bulk form show a mean strength in tension of only about 40 MNm^{-2} . The statistical variation of strength about this figure makes it desirable to allow a substantial safety margin and to design using a figure of about $7 \text{ MNm}^{-2(5)}$.

The strength of glass can be increased to about 200 MNm^{-2} by commercial toughening processes. The use of such glasses is not possible, however, at elevated temperatures since detoughening will occur. Commercial glass fibres display a strength of about 2 GNm^{-2} ; this high figure is dependent upon surface protection, given usually by organic coatings. Removal of the coating will result in a marked decrease in strength.

Elastic modulus Up to the fracture stress, glass behaves, for most practical purposes, as an elastic solid at ordinary temperatures. Most silicate-based commercial glasses display an elastic modulus of about 70 GNm^{-2} , i.e. about 1/3 the value for steel. If stress is applied at temperatures near the annealing range, then delayed elastic effects will be observed and viscous flow may lead to permanent deformation.

The brittle nature of glasses at normal temperatures makes them inappropriate for use in locations where severe impacts are likely to be encountered. In the design of pipelines or other equipment it is possible to use normal engineering assembly techniques provided that suitable gaskets or cushioning are provided at joints and supports and that care is taken in tightening bolts to avoid unequal or localised stresses.

Chemical Properties

Technical glasses are now used so extensively and in such widely varying circumstances that it is necessary to be as accurate as possible in describing their chemical properties. The deterioration of individual glasses is dependent on composition, founding process and use and, unless the degradation processes are accelerated, may only be observable after very long periods of time. A typical figure for the corrosion rate of an ordinary soda-lime-silica glass would be below 0.008 mm/y. The effect is accelerated when the exposure takes place at higher temperatures, e.g. in boiling water or in an autoclave. Table 18.5 compares the corrosion resistance of some commercial glasses.

Table 18.5 The corrosion resistance of some commercial glasses

Glass	1	2	3	6	7
Water	1	2	2	1-2	2-3
Acid	1	2	2	1-2	2-4
Weathering	1	3	3	1-2	2-3

Key 1. Will virtually never show effects.

2. May occasionally show effects.

3. Will probably show effects.

Notes 1. See Table 18.3 for compositions.

2. Table after Hauck, J. E., *Mats. Engng.*, 85, Aug. (1967).

One of the most commonly used measures of durability, i.e. the loss of sodium from the glass, is important to the pharmaceutical and chemical industries, but other changes such as loss of surface quality, are of equal importance for optical and window glasses. The properties of a wide range of technical glasses are well catalogued⁵⁻⁷, but the data are often inadequate when considering a particular application and where possible non-standard 'whole article' tests are advisable.

In selecting a glass for chemical durability or weatherability regard must be paid to the temperature and concentration of the corrosive agent, length of exposure, the ratio of reagent volume to surface exposed and to the mechanical operating conditions. Guidelines on the durability of many commercial glasses in some attacking media are available from standard durability tests.

Glass durability tests There are two types of durability tests for glassware, viz. 'grain' or 'powder tests' and 'whole articles' tests.

Grain tests In these tests, samples of glass, crushed and graded to a specified sieve size, are exposed under standard conditions of time and temperature to the attacking medium. The temperatures commonly used are 98°C (water bath) and 121°C (autoclave) and the attacking media are water, acid and alkali. The amounts of a particular glass constituent (usually soda or total alkali) removed from a standard weight of grains in a given time are determined.

Standard grain tests have been established by various national standards bodies and by some pharmaceutical authorities. The most important of these

standard tests are the American⁸ and the German⁹. Several other continental standards are essentially based on the German. The present British standard¹⁰ relates only to laboratory glassware. The German and American standards differ in a number of details and to try to establish an international uniformity the ISO have issued recommended procedures¹¹. A new British standard in preparation will be based on these procedures.

Careful comparison of results from different laboratories using a particular grain test has shown considerable divergence, and it appears that to obtain consistent results very close adherence to the details of the standard procedures regarding grain preparation, extracting media and analysis is necessary. Nevertheless, grain tests are extensively used, especially in USA and Germany where a further step has been taken of classifying glasses by their 'hydrolytic resistance,' a glass being placed in one of four classes according to the titre of the aqueous extract.

The following examples describe the extraction of alkali by water from 2 g samples at 97.3°C¹² for three glasses of different hydrolytic class.

<i>Glass</i>						
Class I	Time (h)	1	2	3	4	6
	Titre (ml of 0.01N HCl)	0.12	0.20	0.29	0.40	0.54
Class III	Time (h)	0.5	1	2	4	
	Titre (ml of 0.01N HCl)	0.65	0.96	1.39	2.0	
Class IV	Time (h)		1	2	4	
	Titre (ml of 0.01N HCl)		3.0	4.4	6.3	

Whole article tests Grain tests are open to the criticism that they do not necessarily reflect the behaviour of the finished product in service, hence various tests on complete glass articles have been developed. These are normally carried out under accelerated conditions, and on completion various relevant factors are determined, such as loss in weight, alkali or other constituents extracted, the weight of soluble and insoluble materials in the extract and an assessment of surface condition. The advent of the electron microscope as a standard tool has made the latter study much more objective.

Whole article tests are particularly useful in the evaluation of window and optical glasses. Various tests have been proposed for window glass, but no standards exist. The usual procedure is to subject the glass to an accelerated humidity/temperature weathering cycle and to assess the surface conditions after a given period of treatment. The degree of haze formation has been suggested as a method of measuring surface damage, but generally visual comparison with a standard is used. Figure 18.1 illustrates the application of such a test to various optical glasses.

Many optical glasses are much less resistant to attack than are container and window glasses, and less severe tests are necessary. A commonly used method is to immerse specimens in either dilute nitric acid or standard acetate solution of pH 4.6 for specified periods at room temperature, then to examine the surfaces either visually or by interferometry.

Glass fibres present a particular problem. The water resistance of the base glass can of course be measured by a grain test, but this is unlikely to be representative of the performance of the final product. Generally, purely empirical methods are used to test the glass fibres *in situ* in a composite

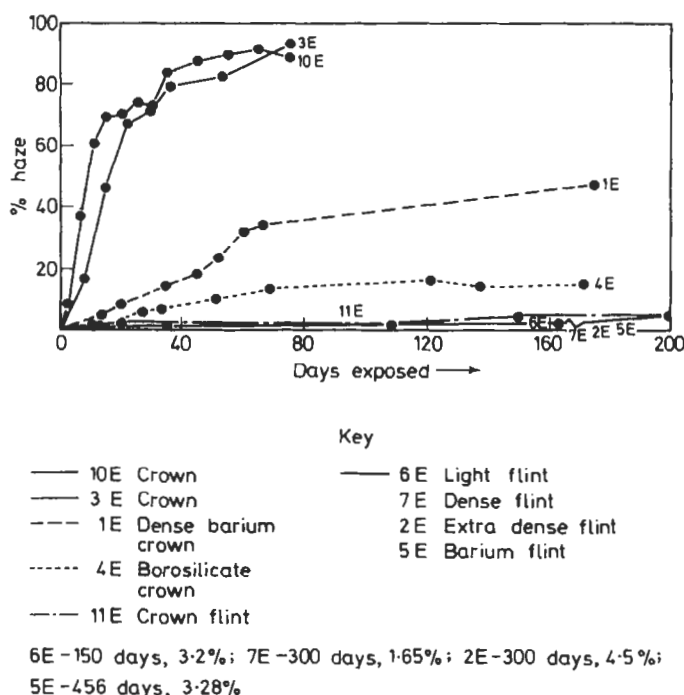


Fig. 18.1 Comparison of optical glasses after exposure to an alkaline solution (after Simpson, H. E., *Glass Tech.*, 37, 249 (1953)¹³)

material, e.g. the fibres are made up into rods or rings with the appropriate partly-polymerised plastic, the composites are then cured under specified conditions and the breaking strength determined after various exposure to water or steam.

A statement of standard tests for glass durability is given in Reference 14.

Glass Durability Testing

Caution is needed in applying the results of general chemical tests for glass durability across a wide spectrum of glass properties. Glass fibre strengths, for example, are sensitive to the physical, as well as the chemical, nature of the environment and should only be assessed by the direct strength measurements in conditions which closely approximate the final application situation⁴⁴.

The effects of corrosion on other properties need similar direct assessment in many cases. However, in the absence of accepted standard tests the BS, DIN, ISO tests for laboratory glassware are often used. At the present time, the British Standard BS 3473 'Methods of testing and classification of the chemical resistance of glass used in the production of laboratory glassware' is being re-issued in six parts, of which the first five parts are identical to recently revised ISO test procedures. There are also corresponding DIN tests in some cases which are very similar. The current situation is:

BS 3473:part 1:1985 ISO 695/1984 DIN 523 22	Identical test procedures. Weight loss test using boiling alkali and glass pieces.
BS 3473:part 2:1987 ISO 719/1985 DIN 12111	Grain test in water at 98°C Measures alkali extracted.
BS 3473:part 3:1987 ISO 720/1985 No DIN equivalent	Grain test in water at 121°C (autoclave). Measures alkali extracted.
BS 3473:part 4:1983 ISO DP 4802/1982 DIN 52 329, 339	Interior surface of glass containers. Water at 121°C (autoclave). Measures alkali extracted.
BS 3473:part 5:1987 ISO 1776/1986 DIN 12116	Resistance to 6 N HCl at 100°C using glass pieces. Measures alkali extracted.
BS 3473/6	Procedure for classifying glass articles according to chemical and thermal properties. Not yet published in its final form. May be adopted by ISO.

Mechanisms of Glass Corrosion

General corrosion properties The glass surface may react with a corrosive agent in one or a combination of the following ways¹⁵:

- (a) By forming new compounds on the surface.
- (b) By selectively losing material from a leached porous layer.
- (c) By continuous dissolution leaving a freshly exposed surface.

Under certain circumstances components may be leached out of the bulk of the glass to leave a new material.

The nature of the glass surface It is widely accepted that the composition of the glass surface is different to that of the interior of the glass, but it is difficult to quantify the difference. Alkali loss during forming, grinding, polishing and surface treatments, affects the structure of the surface, but a more basic difference is brought about by the effect of the unbalanced force fields at the surface on the ions within the glass.

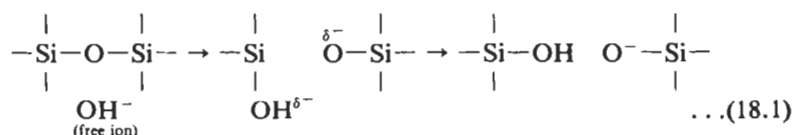
Glass is composed of glass-forming cations (e.g. B^{3+} , Si^{4+} , P^{5+}) surrounded by polyhedra of oxygen ions in the form of triangles or tetrahedra. Two types of oxygen ions exist, viz. bridging and non-bridging. The former, bonded to two network-forming ions, link polyhedra, and the latter, bonded to one network-forming ion only, carry an excess negative charge. To compensate for this, charged cations of low positive charge and large size (e.g. Na^+ , K^+ , Ca^{2+}) are located within the structure. Silicon may be substituted by other cations of large positive charge and small size which are collectively known as *network-formers*.

The difference in size and field strength between ions is reflected in the polarisabilities of each ion, and their final position relative to the glass surface. Since the force field is unbalanced, ions of low polarisability will remain near the surface and ions of higher polarisability will move towards the interior of the glass. A strong feature of chemical reactions associated with the surface is the need to screen adequately (and not merely to neutralise) those cations which have strong electric fields. If the unbalanced force field is removed by the presence of materials, liquid, adsorbed vapour or solid in contact with the glass, there is sufficient mobility within the glass surface zone for it to revert to a more normal structure by the diffusion of ions towards the surface.

Corrosion Mechanisms¹⁶

There is no serious challenge to the view that the alkali or alkaline earth ions are removed from glass in water by an ion exchange process in which H^+ ions diffuse into the glass to preserve the electrical neutrality of the system. However, only under certain circumstances can the rate-controlling process be directly related to the diffusion of sodium in the glass. Most glass/corrosive agent systems are treated as unique cases, since in addition to the concentration of the attacking agent, temperature, rate of flow, and reaction time contribute to what is observed. General chemical principles of electrophilic and nucleophilic types of general attack can be applied to glasses¹⁷. The first is considered as an attack on non-bridging oxygen atoms by reagents with an electron deficiency, and the second as an attack on bridging oxygens by reagents with an electron excess.

For the most common series of corrosive agents, water, steam, acids, alkalis and salts, the hydrolytic processes peculiar to each determine the mechanism of attack. Thus, under the right circumstances, hydrolytic attack on the bridging oxygens* can occur in the following way:



This is an irreversible reaction resulting in permanent damage to the glass network.

The corrosion process is modified by the physical state of the surface. Grinding and polishing processes, in particular, leave the structure in a more open state and with a degree of roughness and residual stress; all can contribute to accelerated corrosion.

The action of water and acids During attack the alkali and alkaline earth network-modifying ions are exchanged by H^+ or H_3O^+ from acid solution.

*It should be noted that the OH^- is partly bonded to the network and has lost part of its charge. The oxygen has acquired a partial negative charge and is only partially bonded to the network. Thus the δ^- indicates a transition state in which the charges on the OH and O lie between 0 and -1.

In some glasses the exchange process can go to completion causing only a small degree of network damage. In water, the exchange process proceeds at a very much slower rate relative to the acid conditions and some attack of the network is possible due to the presence of alkali ions from the glass moving into solution. This is most pronounced when glass is attacked by steam at high temperature and there is no mechanism for the removal of alkali from the hydrolysed zone. Acid solutions mitigate this form of attack by neutralising the alkali as it is formed.

The attack of most glasses in water and acid is diffusion controlled and the thickness of the porous layer formed on the glass surface consequently depends on the square root of the time. There is ample evidence that the diffusion of alkali ions and basic oxides is thermally activated, suggesting that diffusion occurs either through small pores or through a compact body. The reacted zone is porous and can be further modified by attack and dissolution, if alkali is still present, or by further polymerisation. Consolidation of the structure generally requires thermal treatment.

Attack by alkali solution, hydrofluoric acid and phosphoric acid A common feature of these corrosive agents is their ability to disrupt the network. Equation 18.1 shows the nature of the attack in alkaline solution where unlimited numbers of OH^- ions are available. This process is not encumbered by the formation of porous layers and the amount of leached matter is linearly dependent on time. Consequently the extent of attack by strong alkali is usually far greater than either acid or water attack.

Both acids form compounds of silicon as a result of attack on the network, silicon fluoride from hydrofluoric acid and silicic phosphate from phosphoric acid.

Chemical attack by other agents If the hydrogen ion concentration is high enough, the glass loses a substantial amount of weight by leaching, but these reactions are very dependent on the nature of the ions in solution. Certain salts, especially those of Zn, Al and Be, if present as trace amounts, can have a beneficial effect by poisoning the process and preventing the occurrence of leaching.

General Corrosion Behaviour

Important effects on glass durability in aqueous conditions, due to the interrelation between glass composition and environmental pH, have been reviewed recently by Doremus²⁰ and Adams²¹. To some extent, durability can be predicted on thermodynamic grounds. In general, additions of calcia and alumina to a basic alkali silicate glass confer water resistance, additions of zirconium, lanthanum, tin and chromium oxides improve alkali resistance and reducing the levels of boron, aluminium or lead oxides, in glasses where they are present, improves acid resistance. Predictions of the effects of added oxides on glass durability should, however, be treated with caution. Structural factors, such as occurrence of phase separation, coordination state, mixed alkali effect and/or kinetic effects resulting from the presence or absence of insoluble reaction product layers on the glass surface, can influence durability to a significant extent.

More generally, Valez et al.²⁴ have reviewed the corrosion behaviour of silicate and borate glasses in contact with alkali metals and molten salts, as well as in aqueous conditions.

Another important aspect of glass corrosion behaviour which should be emphasised is the effect of applied stresses. As with most other brittle solids, glass is subject to stress-enhanced corrosion—often described as ‘static fatigue’. Under a continuously applied stress, and in the presence of normal environmental moisture (or other more aggressive corrosion conditions), cracks may grow from flaws on the glass surface and this can lead to delayed failure at stresses below the strength level which is measured in a short-term loading test^{23, 26}. As a consequence, common silicate glasses are usually expected to have a load-bearing capacity at one-quarter to one-third the short-term strength when continuously loaded over some 50 years in the normal atmosphere.

The Cleaning of Glass

There is no universally ideal technique for either cleaning glass or avoiding contamination of the surface. In the most severe circumstances of corrosion the only methods capable of restoring an acceptable surface finish consist of grinding and polishing or removing the contamination and corroded layers by strong etching agents such as hydrofluoric acid. Less severe conditions may respond to treatment by various detergent solutions or organic solvents, these being considerably aided by ultrasonic vibration. Manual washing or ultrasonic cleaning can be used to remove massive dirt accumulations. The vapour degreasing process, which uses isopropyl alcohol, has minimal corrosive action on the glass.

To restore old stocks of corroded glass, treatment in hot 1% sodium hydroxide solution followed by rinsing in 5% hydrochloric acid and a final rinse in pure water at room temperature is recommended¹⁸.

New Developments in Applications

Over recent years, a number of new applications of glasses have grown out of increased understanding and control of glass corrosion behaviour.

Conventional silicate and borosilicate glasses are subject to severe corrosive attack in highly alkaline solutions (pH 12–13.5) such as those found in hydrating Portland cement. There is rapid and drastic loss of strength in fibres formed from glass compositions such as no. 2 or no. 9 of Table 18.3. Highly alkali-resistant glass fibres have been developed from silicate glass compositions containing about 16 wt% of zircona^{27, 28} and these have formed the basis for development of a range of glass-fibre reinforced cement (GRC) materials, analogous to glass-fibre reinforced plastics (GRP). In the GRP field, it has been shown that *E*-glass borosilicate fibres (composition no. 9, Table 18.3) are prone to strength loss and stress corrosion in acidic environments^{29, 30}—this in turn led to the development of an acid-resistant version of *E*-glass for use in such conditions³⁰.

In the flat/container glass fields a wide range of surface treatments now exist which modify the surface of the glass to confer corrosion or abrasion resistance, improve mechanical strength or optical properties. A number of treatments which claim to improve chemical or corrosion resistance are described in References 31 to 35.

The slow rate of dissolution of, or leaching from, durable glasses has led to proposals for the vitrification of nuclear waste. Glasses based on the sodium borosilicate system appear to be favoured because of their ability to dissolve the waste, combined with good chemical durability. Intensive development has taken place over recent years²¹ and a regular journal is devoted to this topic³⁶.

The above applications depend on the development of corrosion-resistant glasses. Equally interesting new developments depend on the controlled use of glass corrosion/dissolution. For example, glasses based on the network formers, P_2O_5 and B_2O_3 , have been formulated which even at a low pH react with attacking media by continuous dissolution at a constant rate leaving a freshly exposed surface. Heavy-metal ions incorporated in the glass are therefore released into the attacking medium at a controlled rate governed by the composition of the glass. The patent literature describes several uses of these types of glass, e.g. as biocides, as corrosion inhibitors and in animal husbandry³⁷⁻⁴⁰. Phosphate glasses, both in solid form or as a powder component in cements⁴¹, have been used to provide the trace elements Cu, Co, Se to ruminant animals. More recently, polymer bonded soluble phosphate glass boluses have been developed to control breeding activity in sheep by releasing the hormone melatonin into the rumen⁴². In a further application of 'controlled release' of glass components, glass ionomer cements have been used for dental cements, surgical splinting and foundry sands. These cements are based on the hardening reaction which occurs between a powdered ion leachable glass and aqueous solutions of homo-plus co-polymers of acrylic acid⁴³.

Glass-Ceramics

Definition and Properties

Glass-ceramics are a family of materials that are polycrystalline in nature and are formed from the liquid or glassy state. A glass-ceramic article is made by the heat treatment of a vitreous body in two stages:

1. Nucleation. The glass is held at a temperature below its softening point for a period of minutes or hours to allow nuclei to develop.
2. Crystallisation. The temperature of the nucleated glass is raised to just below the softening point when crystals form and grow around the nuclei.

Ideally the product is a fine-grained ceramic containing interlocking crystals with sizes ranging from less than 10 nm in transparent glass-ceramics to several micrometres, with a residual, usually small, glass content. The behaviour of the material is largely determined by the choice of the cry-

stalline phase; by suitable choice a range of useful properties has been obtained¹⁹.

As a class of materials, glass-ceramics have the following general characteristics:

1. Impervious, with moderate densities similar to those of glasses.
2. Rather high strengths for oxygen-rich solids, accompanied by some scatter of individual values.
3. Stiff, elastic, fully Hookean behaviour.
4. Considerable hardness and resistance to abrasion.
5. Chemical stability and resistance to corrosion.
6. Resistance to medium-high temperatures (higher temperatures than most glasses but lower than the refractory oxides) and low thermal conductivity.
7. Resistance to the passage of electrical current.

Special characteristics can be developed in individual materials depending on the cations present and their arrangement relative to each other and to the oxygen anions. The most important of these characteristics is low, medium or high reversible thermal expansion. The properties of some commercially available glass-ceramics are summarised in Table 18.6.

Chemical Durability of Glass-ceramics

Although the factors which govern the chemical stability of glasses are fairly well-known, there is little information concerning this aspect of glass-ceramics. While the chemical behaviour of a glass-ceramic is strongly influenced by the chemical composition of the parent glass, several different crystalline compounds together with a residual glass phase are likely to be present. The relative resistances of these phases to attack by water or other reagents will determine the chemical stability. In general, a glass which exhibits poor chemical stability is unlikely to give rise to a glass-ceramic of high stability. To this extent the factors which govern the stability of glass-ceramics can be equated to those which determine the chemical stability of glasses.

In most cases, glass-ceramics possess good chemical stability and certainly compare favourably in this respect with other ceramic materials. Table 18.7 summarises makers' data for chemical attack on commercially available materials.

Certain types of glass-ceramic have good resistance to attack by corrosive chemical reagents. Low-expansion glass-ceramics derived from lithium-aluminosilicate glasses are only slightly inferior to borosilicate chemically-resistant glass with regard to attack by strong acids and are somewhat more resistant to attack by alkaline solutions. Materials derived from magnesium-aluminosilicate glass compositions are slightly less resistant to attack by strong acids and alkalis than are chemically-resistant borosilicate glasses. Even at high temperatures these types of glass-ceramic retain resistance to attack by corrosive gases.

For certain applications it is important that the glass-ceramic should be unaffected by contact with reducing gases at high temperatures. In such

Table 18.6 Property data for some commercially available glass-ceramics

	<i>Units</i>	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>	<i>F</i>
Specific gravity	g/cm ³	2.55	2.5	2.53	2.5	2.5	2.7
Average thermal expansion coefficient	$\times 10^{-7} \text{ deg C}^{-1}$ (100°C-300°C)	6	12.7	97	4.2	-3	90
Transition point	°C	820					
Softening point	°C	950			1 250		
Maximum service temperature	°C	800	1 000	1 500		814	
Bending strength	$\times 10^{-7} \text{ Nm}^{-2}$	12	18	8.8	11	13	25
Volume specific resistance	log (Ωcm)	10.6	10.6	6.7	10	11.6	
Compositional type		lithium alumino silicate	lithium alumino silicate	potash magnesia alumino silicate	lithium alumino silicate	lithium alumino silicate	sodium baria silicate

Key: *A* Heatron T (Trade name of Fuji Photo Film Co. Ltd.)*B* Neoceram-15 (Trade name of Nippon Electric Glass Co. Ltd.)*C* Corning code 9650 (Machinable glass-ceramic)*D* Pyroceram 9608 (Trade name of Corning Glass Works)*E* Hercuvit (Trade name of Pittsburgh Plate Glass Co.)*F* Centura ware (Trade name of Corning Glass Works)

Table 18.7 Chemical resistance data for some commercially available glass-ceramics

Chemical resistance	Units	A	B	C	D
<i>Powder method</i>					
Water solubility	mg as Na ₂ O per 1 mg sample	0.29			
Acid solubility	loss in wt., %	0.06			
Alkali solubility	loss in wt., %	0.13			
<i>Surface method</i>					
H ₂ O (90°C × 24 h)	mg/cm ²	0.00			0.12
5% HCl (90° × 24 h)	mg/cm ²	0.13	0.8	128	0.1-0.3
5% NaOH (90° × 24 h)	mg/cm ²	0.04	3.5	5	0.02-0.1

Key: A Heatron T
 B Neoceram-15
 C Corning code 9650
 D Pyroceram 9608
 E Herculit

cases the composition must not include any oxides such as lead which are easily reduced to the metal.

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18.3 Vitreous Silica

Introduction

Vitreous silica, also referred to as quartz glass, fused quartz, or fused silica, is a material of considerable importance, possessing a unique combination of high softening temperature, excellent resistance to chemical attack, and high transparency. The general physical and mechanical characteristics are common to all glasses, and have been reviewed adequately in Section 18.2, the difference being that the high purity ($>98.7\%$ SiO_2) maximises the durability, fusion temperature and volume stability.

The superiority of fused silica over conventional glasses is illustrated in Table 18.8.

Table 18.8 Physical property data for fused silica, crown glass and pyrex

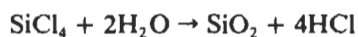
	Fused Silica (SiO_2)	'Crown' glass ($\text{SiO}_2\text{-Ca-Na}_2\text{O}$)	Pyrex ($\text{SiO}_2\text{-B}_2\text{O}_3\text{-Na}_2\text{O}$)
Softening point ($^{\circ}\text{C}$)	1 594	720	820
Annealing point ($^{\circ}\text{C}$)	1 082	540	565
Resistivity (Ωm)	10^{15}	1.1×10^{13}	10^{15}
Dielectric constant at 1 kHz	3.8	7.4	5.1
Thermal expansion $\times 10^{-7} \text{ K}^{-1}$	5.4	8.8	3.3

Manufacturing Process

The raw materials for the production of vitreous silica are either high purity rock crystal from which the transparent form is produced, or vein quartz (high grade glass sand) from which impurities have been removed by acid leaching. The persistence of liquid and gaseous inclusions is partly responsible for the translucency of the cheaper form of vitreous silica. The ground quartz is melted at around 2000°C by induction heating in a graphite crucible. Even at this temperature, the melt viscosity is so high ($10^5\text{--}10^6 \text{ Pa s}$) that the trapped gas bubbles cannot be removed by ascent to the surface. Therefore gases from the intergranular spaces are removed by evacuation

to high vacuum at the beginning of sintering ($\sim 1400^{\circ}\text{C}$) to allow pores to be closed completely. At high temperature, the pressure cannot fall below the equilibrium vapour pressure, which is comparatively high as a result of partial reduction to SiO .

Vitreous silica produced by this route contains small amounts of impurities such as Fe, Cr, Al and Ca. To achieve metal ion impurities $< 10^{-7}\%$ the synthetic hydrolysed silane process is used. Organic silica compounds or SiCl_4 are hydrolysed in a flame to produce fine molten droplets of SiO_2 which is deposited on a cold base.



Contamination by hydroxyl groups is eliminated if oxygen is used instead of water in the reaction.

Structure and Physical Properties

Polymorphism of Silica

Although vitreous silica is nominally a homogeneous isotropic amorphous material, and should normally remain so during its service life, it is in fact in a metastable condition. The tendency to revert to crystalline forms with attendant deterioration in mechanical durability places severe limitations on the range of applications. Figure 18.2 illustrates the polymorphic forms of silica, and the dimensional changes accompanying each transition.

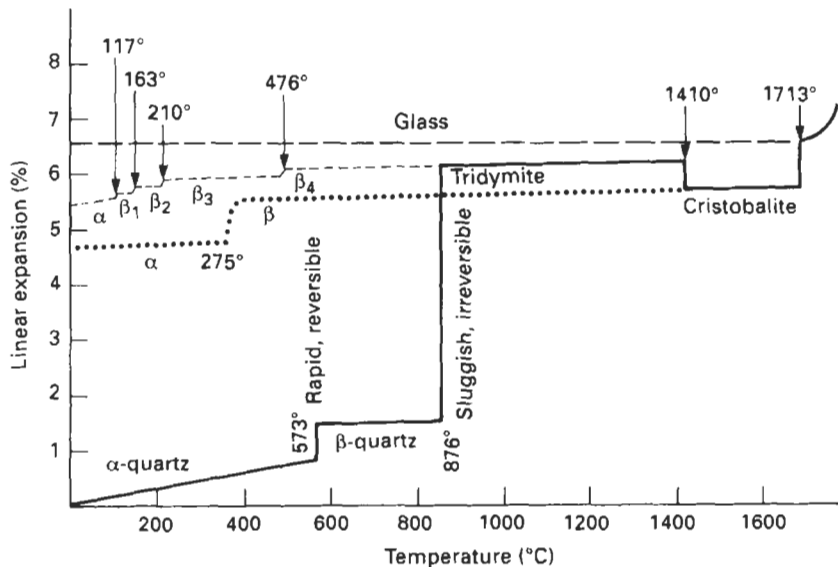


Fig. 18.2 Polymorphism and dimensional changes in silica as a function of temperature

Changes from one polymorphic form of crystalline SiO_2 to another, as from tridymite to quartz at temperatures below 870°C and to cristoballite above 1470°C , involve the breaking of very strong $\text{Si}-\text{O}$ bonds. High energies are required for these 'reconstructive' changes, and changes from one form to another require very long periods for completion. On the other hand, inversions from high to low temperature forms of quartz or cristoballite involve only changes in the angles between adjoining SiO_4 tetrahedra, and these 'displacive' transformations are accomplished almost instantaneously. The accompanying volume changes lead to disruption of ware containing significant amounts of quartz or cristoballite.

Thermal Expansion

The coefficient of thermal expansion of vitreous silica is very small (5.4×10^{-7} over the range $0-1\,000^\circ\text{C}$), about one-sixth that of porcelain. It is thus highly resistant to thermal shock.

Heat Resistance

Being a glass, vitreous silica softens progressively as it approaches its melting point of $1\,713^\circ\text{C}$. The maximum recommended working temperature is $1\,050^\circ\text{C}$ in an oxidising atmosphere, though it may be taken to $1\,350^\circ\text{C}$ for short periods. Surface devitrification to cristoballite occurs above this temperature. This causes some loss of transparency, but chemical and mechanical durability are unaffected provided the temperature does not fall below the β to α inversion temperature (275°C), which would lead to the initiation of cracks. It should be noted that devitrification is accelerated by traces of alkali metal compounds, particularly potassium and lithium salts, sodium tungstate and ammonium fluoride. Devitrification is also enhanced by water vapour and oxygen, but inhibited by neutral or reducing atmospheres.

Thermal Conductivity

The thermal conductivity of fused silica is low ($1.38 \text{ W m}^{-2} \text{ K}^{-1}$). The transparent form passes infra-red radiation with little loss up to wavelengths of $3.5 \mu\text{m}$.

Electrical Characteristics

The insulating properties are excellent. At ordinary temperatures the resistivity of the translucent form is $10^{15} \Omega\text{m}$, and it is capable of withstanding high-frequency discharges at high voltages. See also Table 18.4 for data on other physical properties.

Resistance to Chemical Attack

Most glasses suffer chemical attack and deterioration due to ion exchange of sodium ions to form a highly alkaline solution which subsequently attacks the network. As network-modifying oxides are absent from fused silica, this mode of attack does not occur. Hence fused silica is highly resistant to most aqueous solutions, even aqua regia at elevated temperatures having no effect. Only those reagents that attack the network silica directly, such as strong alkalis and fluorides, are to be avoided.

Boiling Water and Steam

There is negligible reaction with water and steam at moderate temperatures and pressures, as indicated by the free-energy change for the solution reaction:



A solubility of <6 ppm occurs, however, at temperatures in the range 400–500°C and pressures of the order of 3.5 MNm^{-2} . The solubility rises to 0.14% for the translucent form, and 0.035% for the transparent.

Fluorine, Hydrofluoric Acid and Alkaline Solutions

Silica is susceptible to attack by all three reagents, the rate of corrosion increasing with temperature and concentration. Hence 5% caustic soda solution can be contained in fused silica at room temperature, but attack becomes significant at pH values greater than 9, as shown in Fig. 18.3.

The essential step in the dissolution reaction is the breaking of a siloxane bond $\text{Si}-\text{O}-\text{Si}$. This bond, although strong, is polar, and may be represented as $(\text{Si}^{\delta+}-\text{O}^{\delta-})$. The excess positive charge associated with the

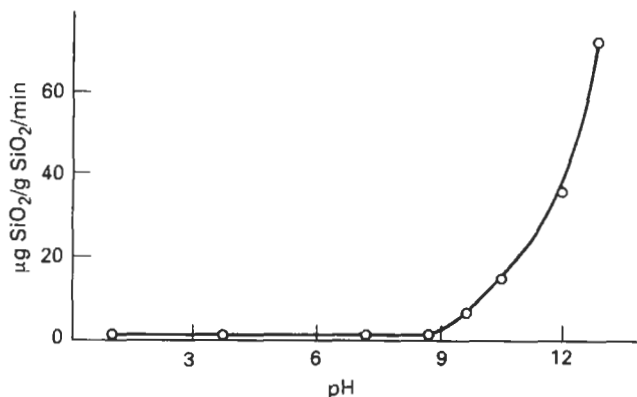
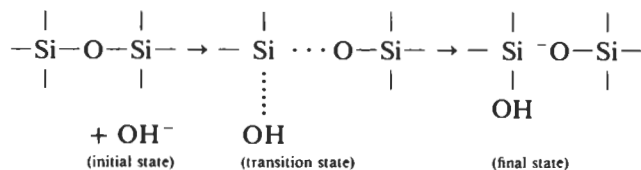
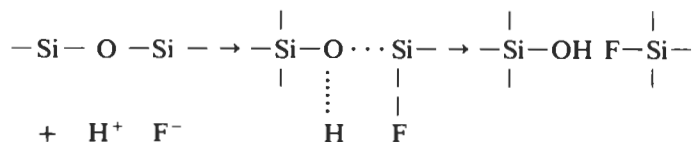


Fig. 18.3 Effect of pH on the rate of silica extraction from vitreous silica powder at 80°C (after El-Shamy and Douglas, 1967)

silicon atom makes it susceptible to attack by nucleophilic reagents such as the OH^- ion which attaches itself to the silicon, rupturing the network at that point as shown below:



The attack of HF is thought to proceed by a similar mechanism in which there is simultaneous nucleophilic and electrophilic attack on the network silicon and oxygen atoms, respectively, according to:



It should be pointed out the H^+ ion alone is insufficiently powerful to affect disruption of the siloxane bond without the simultaneous action of the F^- ion. Consequently sulphuric and nitric acid do not initiate attack, even at temperatures up to $1\,000^\circ\text{C}$. Exceptions to the principle are hydrochloric and hydroiodic acid, which, although satisfying the requirements of simultaneous nucleophilic–electrophilic attack, exert a negligible degrading effect on silica.

Sodium fluoride also attacks silica, as do sodium metaphosphate and sodium polyphosphate, and to a lesser extent sodium carbonate and sodium cyanide. Attack is particularly vigorous for fused alkalis, alkali halides and phosphates.

Basic Oxides

As an acidic oxide, SiO_2 is resistant to attack by other acidic oxides, but has a tendency towards fluxing by basic oxides. An indication of the likelihood of reaction can be obtained by reference to the appropriate binary phase equilibrium diagram. The lowest temperature for liquid formation in silica–oxide binary systems is shown below:

Oxide	Al_2O_3	BeO	CaO	MgO	ThO_2	TiO_2	ZrO_2
eutectic($^\circ\text{C}$)	1 546	1 670	1 436	1 543	1 700	1 540	1 675

Metals

Silica is only decomposed by those metals which have a high affinity for oxygen as indicated by the Ellingham diagram (Fig. 18.4). On this basis, molten sodium should be compatible with silica:

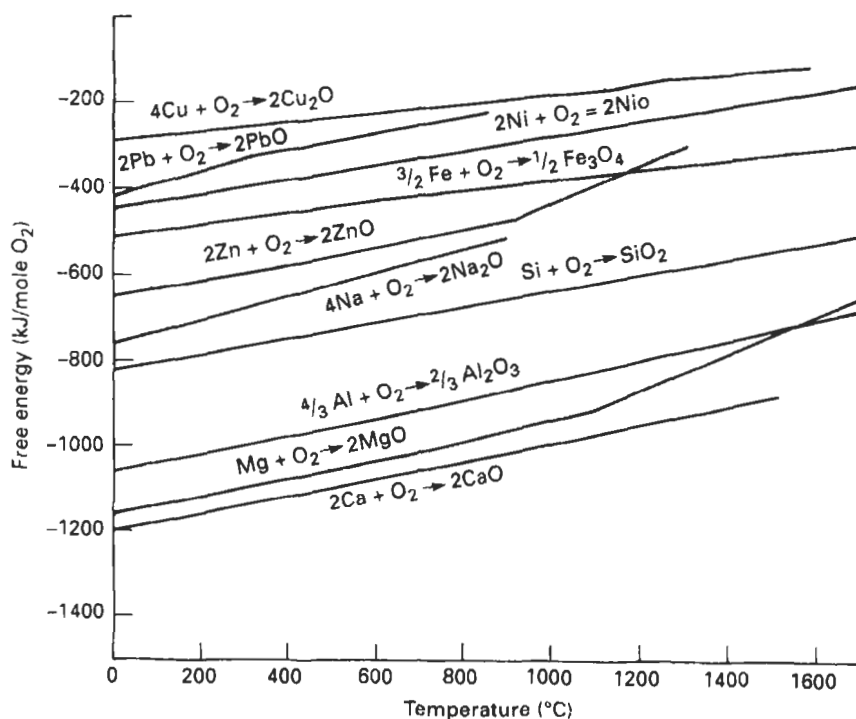
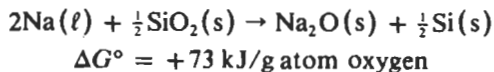


Fig. 18.4 The standard free energy of formation of various oxides as a function of temperature



The equilibrium levels of the reaction products are very small, but both can dissolve in liquid sodium, and sodium oxide can form compounds with silica. As a consequence, the reaction moves to the right, leading to further reduction of silica. Nevertheless, vitreous silica crucibles have been used successfully for containing molten antimony (850°C), copper (1210°C), gallium (1100°C), germanium (1100°C), lead (500°C) and tin (900°C).

In accordance with the free energy diagram, silica is readily attacked by molten aluminium, lithium, magnesium and calcium.

Applications of Vitreous Silica

The high thermal and electrical resistance of vitreous silica, and its imperviousness to chemical attack, make it suitable for a wide range of applications. These include chemical and physical laboratory ware, tubes and muffles for gas and electric furnaces (including vacuum furnaces), pyrometers, insulators for high-frequency and high-tension electrical work, mercury-vapour and hydrogen-discharge lamps, high-vacuum apparatus, plants (complete or partial) for chemical and related industries, equipment

for the manufacture of pure chemicals, tubes, chimneys and radiants for the gas- and electric-heating industries, component material in refractory and ceramic mixtures, etc.

It is used for pipes to carry hot gases and acids, acid distillation units, condensing coils, S-bend coolers, hydrochloric acid cooling and absorption systems, nitrating pots, and cascade basin concentrators for sulphuric acid. The inertness of vitreous silica to most acids is also utilised in the manufacture of electric immersion heaters and plate heaters for acidic liquors in chemical processes and electroplating baths. Vitreous silica wool is used for filtration of acidic liquids and filtering hot gases. The resistance of vitreous silica to water and steam at normal temperatures and pressures makes it applicable in the production of pure water for the manufacture of highly purified chemicals. Because of its thermal properties, it is used for the construction of muffles of oval cross-section used for the bright annealing of metal strip and wires.

Special products include transparent vitreosil springs, which are ideal for continuous measurement in corrosive atmospheres, and quick-immersion thermocouple protection sheaths for rapid temperature measurement.

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18.4 Glass Linings and Coatings

While glass can provide many of the desirable features of an ideal inert material, fabrication difficulties prevent its use for large-diameter chemical process equipment, and mechanical considerations would in any case make it necessary to treat any such equipment with great care.

The high chemical resistance, and the non-toxic, non-flavouring and thermal-resistance properties of glass, can however be combined with the mechanical strength of metals by covering metal surfaces exposed to corrosive media with a layer of suitable glass. It thus becomes feasible to produce large storage or transport tanks of over 10 000 litre capacity, reaction vessels, valves, pipes, silos, smoke stacks, car exhausts etc. which have this serviceable combination of properties.

The principal advantages of glass linings are the increased size and mechanical strength that are possible compared with all-glass equipment, and the flexibility of operation with different chemicals compared with all-metal equipment. The increased heat transmission, in comparison with glass equipment, can also be an advantage.

The principal disadvantages are the loss of transparency and the potential vulnerability of the lining to mechanical damage unless sensible precautions are taken in handling, installation and service. A variety of metals can be protected in this way, including copper, gold, stainless steel, titanium and uranium, but by far the most extensive use of the technique is for steel equipment.

Glass Preparation

There are a number of proprietary glass formulations for coating steel. In most cases the chemical constitution has not been disclosed but the more successful types are borosilicates containing more aluminium and alkali oxides than the typical heat-resisting borosilicates discussed in Section 18.2. In formulations, for ground-coating the steel, the glasses contain a much greater proportion of cobalt oxide than is found in ordinary glasses, to encourage the formation of a bond between the metal and the glass. The coefficient of linear expansion of a typical glass for this application is about $10 \times 10^{-6}/^{\circ}\text{C}$. The disparity between this figure and the higher expansion coefficient of the steel is quite deliberate and results in the development of

compressive stresses in the glass layer after processing. The stress which develops gives more resistance to thermal shocks or external stresses than if the expansion of the glass and steel were accurately matched. The second coat, or cover-coat, has a composition different from the first coat, or ground-coat, such that it has optimum durability.

The raw materials required to produce the particular glass composition are intimately mixed and melted at a temperature near 1300°C. The melt is quenched with water, yielding the glass in a granular form known as *frit*, which is subsequently either ground to give dry glass powder or wet-milled with ball clay to form a creamy slip. It can be applied to the steel in either form, the particular method depending on the design and size of the structure.

Metal Preparation

A low-carbon (less than 0.2% C) steel is usually employed in the manufacture of chemical storage or process vessels, water heaters, and the like; one writer refers more precisely to "a rimmed steel (ASTM A285), grade *A* or *B* flange quality" as being suitable, and states that with this base, defects such as fishscaling, blistering, crazing and poor adhesion are avoided. Cast iron is frequently employed in such equipment as valve bodies and pipe unions. It should be good quality, close-grained grey iron free from blow-holes, cavities and porosity. 'Filling' is not permissible.

Conventional welding techniques are used in fabrication and assembly of the steel body, but special precautions must be taken to ensure that the weld metal is of similar composition to the base metal, and that moisture-(hydrogen-) free electrodes are used. Lap-welded joints and riveted structures are not suitable for the subsequent enamelling operations; butt welding is much preferred. The completed assembly is examined in detail to check defects likely to impair serviceability, and is then normalised at 900°C to relieve stresses set up during fabrication. The heat treatment also has the advantage of burning-off any organic contamination. After cooling, the vessel is sand-blasted with a silica-type grit to remove oxide scale and to promote, by providing a roughened surface, mechanical keying of the glass ground-coat layer to be applied. The expensive preheating to burn off grease can be replaced by chemical descaling and degreasing¹. Subsequently an alkaline cleaner, followed by a water wash and then by an acid pickle (HCl or H₂SO₄) and rinse prepares the steel for enamelling. A nickel dip^{2,3} can be used to further enhance adherence.

Points which manufacturers note as being important in the design of these vessels are as follows:

1. The metal thickness should be as uniform as possible throughout, avoiding heavy bosses, lugs or brackets.
2. The minimum radius recommended for all curved surfaces is 6.4 mm; sharp edges must be entirely avoided. On small radii there is a risk that shaling or other difficulties might arise.
3. The risk of distortion on firing is greater if the design calls for numerous apertures in the vessel or its cover.

Lining Processes

The ground coat, where used, is sprayed on in the form of a wet slip and after drying is fired at approximately 900°C. With open vessels or small cast-iron units, dry glass powder can be dusted directly on to the hot, fused surface of the ground coat; larger vessels such as storage tanks are allowed to cool, inspected and then sprayed uniformly with the wet slip. The coating is thoroughly dried and then fused by heating the vessel in a furnace at approximately 850°C. The vessel is cooled, and further coats of glass enamel may be applied as required in the same way. Thicker layers can thus be built up. Many cast iron items are preheated to 800°C to 1 000°C and dusted with enamel powder. The coherent glass coating develops immediately and consolidates as the item is returned to the kiln for a slow cool. It is clearly important that the vessels being treated should not distort under their own weight during furnace treatment, and it may be necessary to design the article with slightly greater thickness than usual to allow for the softening effect of high temperatures. Another way of avoiding the difficulty with closed vessels is to force inert gas into the tanks at controlled pressure. The integrity of the linings is tested electrically.

Properties of Glass Linings on Steel

Mechanical Properties

With correctly formulated glass, the lining has the ability to withstand stresses up to the elastic limit of the steel without breaking. Impacts sufficiently severe to dent the steel will probably cause fractures in the lining. The hardness and abrasion resistance of the lining are similar to those of all-glass equipment and a smooth, easily cleaned surface is produced. The combined effect of mechanical keying of the glass to the metal and the chemical bond developed between the two results in a very high adhesive strength. Test figures indicate that the bond strength is of the order of 35–70 MN/m².

Thermal Properties

The thermal shock resistance of glassed steel, i.e. the safe limit of temperature difference between the glass surface of the vessel and any charge introduced, varies according to the general operating temperature. This is because the desired compressive stress on the glass is reduced as the temperature increases. With a typical coating formulation on a vessel operating at 120°C, the recommended maximum thermal shock would be about 93°C, while at an operating temperature of 205°C the corresponding figure would be 55°C. Recent improved formulations have made it possible for vessels to withstand thermal shocks of some 30% greater than this. Plant can operate from –20°C to +300°C with the maximum operating temperature being determined by the corrosivity of the contact liquor.

The heat-transfer coefficient for heating in glass-lined equipment is of the order of $340\text{--}455\text{ W m}^{-2}\text{C}^{-1}$, but can be increased by agitation. For cooling, corresponding figures would be $200\text{--}285\text{ W m}^{-2}\text{C}^{-1}$. The numerical values depend on the thickness of the glass coating, increasing with decreasing glass thickness, and the figures quoted represent the behaviour of an average coating.

Chemical Properties

The general pattern of chemical resistance of glass linings is very similar to that of all-glass equipment. Water absorption is negligible, resistance is very high to all acids except hydrofluoric and (at high temperatures and concentrations) phosphoric acid, attack by water is measurable only with difficulty, most organic liquids produce no measurable effect and strongly alkaline solutions are satisfactorily handled at near-ambient temperatures, but at higher temperatures there may be appreciable reaction. For most types of glassed chemical plant the enamel can be assessed by measuring the loss in weight per unit area when exposed to liquid.

Conditions in service vary widely. Many cold liquors (milk and beverages) have little corrosive action and the chosen glass lining need not be very acid resistant. Alternatively, glass-lined reactors and stills might be exposed to high temperatures, under pressure (or vacuum) and the enamel then must be very resistant. A degree of resistance to alkali is always desirable for defence against caustic cleaning aids.

Priest⁴ has given the results of 15-day tests on a particular glassed steel, both for immersion and vapour-phase conditions, in a variety of media. Some of this information is extracted in Table 18.9

Table 18.9 Corrosion of glassed steel in boiling acid/distilled water systems

Test solution	Corrosion rates (mm/y)	
	Liquid phase	Vapour phase
Distilled H ₂ O	< 0.025	0.241
50 p.p.m. HCl	< 0.025	0.163
500 p.p.m. HCl	< 0.025	0.033
1.0% HCl	< 0.025	< 0.025
10.0% HCl	0.040	0.036
14.0% HCl	0.030	0.079
18.0% HCl	< 0.025	0.013
50 p.p.m. H ₂ SO ₄	< 0.025	0.015
500 p.p.m. H ₂ SO ₄	< 0.025	0.043
1.0% H ₂ SO ₄	< 0.025	< 0.025
10.0% H ₂ SO ₄	0.043	< 0.025
20% H ₂ SO ₄	0.033	< 0.025

The effect of temperature on alkali corrosion is illustrated by data from this paper in Table 18.10. There are various glass compositions in service and it is important to ensure that the lining is appropriate for the particular

Table 18.10 Corrosion of glassed steel in alkaline media as a function of temperature

Test solution	Approximate corrosion rates (mm/y)				
	27°C*	38°C	54°C	66°C	82°C
1% NaOH	0.0114	0.0254	0.0889	0.2032	0.533
1% Na ₃ PO ₄	0.0102	0.0203	0.0635	0.1143	0.457
1% Na ₂ CO ₃	0.0076	0.0152	0.0457	0.0889	0.305

* Extrapolated using Arrhenius relationship.

Table 18.11 Corrosion resistance of glass linings

Test solution	Temp (°C)	Duration of test (days)	Corrosion rate (mm/y)		Estimated life of 0.91 mm-thick lining (years)	
			AR	AAR	AR	AAR
Buffered NaOH, pH 11.5	100	30	0.305	0.0762	3	12
0.5% NaOH solution, pH 13	75	30	1.168	0.305	0.8	3
20% HCl solution	Boiling	30	0.01626	0.02108	56	43

processes to be operated. An example of the behaviour of two different types of glass is given in Table 18.11.

Clearly the AAR glass is more preferable to AR for alkaline reactions but is only marginally less resistant to the acid solution; glass AAR can be used up to pH 12 at 100°C.

Enamel Behaviour in Service

Enamels, though alkaline liquor resistant, are not necessarily detergent resistant. Weight loss from enamelled iron surfaces has been related to resistance to detergent attack⁵, but field assessment of the effect of alkaline materials upon enamel⁶ does not always agree with accelerated laboratory tests. British Standard 1344 describes methods for testing vitreous enamel finishes. British Standard CP 3003:Part 2 gives guidance on the selection, design, application, inspection and testing of items to be glass enamelled. This code is not intended for less exacting (domestic) applications.

An apparatus for testing enamel with acid and alkaline liquids (and their vapours) was later proposed⁷ in an attempt to standardise corrosion ratings on an international basis. After surveying enamel properties and their relationship with resistance to liquids of different pH values, the concept of modifying the resistance by including specific elements in the glass structure has been outlined⁸.

For a hot water environment general guidance can be given for the desirable properties in good enamels. Five factors⁹ affecting enamel life are corrosiveness of contact liquor, design, operating conditions, life of sacrificial anode (if any) and the durability of the enamel coat. This implies that

there is no simple accelerated test for determining water resistance, unlike assessing resistance to acid and alkali. Field tests are preferred.

Using present ideas of glass structure, frits can be formulated to have maximum durability. Zirconia enamels have a lower than optimum acid resistance, but titania enamels have superior durability at low pH values. Encouraging crystallisation in the enamel enhances mechanical strength and therefore chemical resistance¹⁰ by reducing the incidence of damage sites which act as foci for attack. The addition of an extra (clear) coat on to the top most coat of enamel gives superior chemical resistance¹¹.

As a future alternative to glassed steel there is ceramics-coated steel which is resistant to abrasion, corrosion *and* high temperatures. The base metal is coated with silicon nitride formed *in situ*. Silicon nitride has resistance to both acid and alkali and it is durable at temperatures up to 1 000°C, suggesting a promising future coating in aggressive operating environments.

General Aspects of Glass Enamel Corrosion

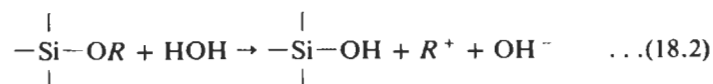
Evidence came from the results of work developing corrosion-resistant glassing compositions about the interaction of liquids with glass surfaces, and there is now a better understanding of the mode of chemical attack on glass. Reaction at the glass surface occurs by ion exchange, dissolution and absorption. Signs of these reactions are a dimming of gloss, thin film interference colours and surface pitting on general degradation. Eventually the corrosion becomes apparent as a loss of gloss. Assessment of gloss by instruments will detect corrosion before it becomes noticeable to the unaided eye¹².

Continued penetration of the glass structure by some ions could lead to its decomposition. The thickness of the ion-exchanged surface layer is related to the durability of the glass¹³. Initial reactions are rapid^{14,15,16}.

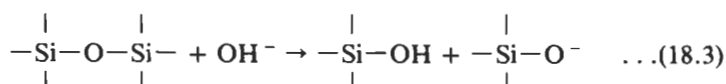
The borosilicate glasses on coated steels contain silica and alkali metal oxides, and the reactions can be considered as involving silicate networks¹⁷. Attack begins as an interaction between silicate lattice ions and protons from the liquid with the consequent leaching of monovalent and divalent ions. Chelating agents sequester polyvalent cations and, if present in an attacking liquid, can increase the rate of attack on the glass¹⁸. The cations Mg^{2+} , Ca^{2+} , Al^{3+} , Zr^{4+} and Ti^{4+} are known to stabilise the siliceous surface film and so aid corrosion resistance, but in the presence of say, ethylenediamine-tetraacetic acid (EDTA), with which these ions react, this protective action is increasingly nullified as the ions are removed from the silicate surface. Complexes are formed between Si^{4+} and some organic acids, notably gallic acid and tannic acid.

Attack by Water

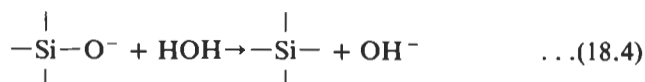
Initially there is the replacement of an alkali ion (R) in the glass by a proton (H) from the water,



The released hydroxyl ion interacts with the siloxane bond in the vitreous network



This open oxygen interacts with a water molecule,



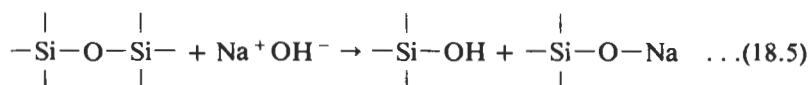
The resulting hydroxyl ion is available for the reaction in equation 18.3.

As the hydrogen ions replace alkali (R) ions a surface film forms which has properties different from the massive glass. This film swells, acting as a barrier to further diffusion of ions into, and out of, the surface, inhibiting further attack. If this layer dries out, the thin film gives characteristic iridescent interference colours.

Where glass linings are exposed to water or steam at temperatures above 150°C the plant manufacturers should be consulted.

Attack by Alkali Solution

With the migration of alkali ions (R^+) into the leachant the attack is no longer by water. If R^+ is sodium the attack on the glass is:



Alkali ions in solution increase the pH, with two consequences. The rate of silica extraction increases with the rise in pH value above 9¹⁹ and the rate of alkali exchange is reduced. However, since the higher alkalinity favours solution (of silica) further alkali is released by the lattice. The quantity of alkali extracted can be used as a measure of the resistance of glass to attack²⁰.

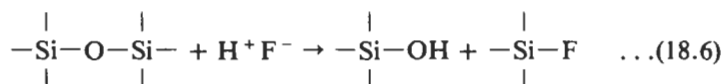
Effect of Leaching Temperature The quantity of alkali extracted in a fixed time increases with increasing temperature. Depending upon the composition of the glass coating and the alkali present (ions of different size behave characteristically), the amount leached approximately doubles for each rise in temperature of 10°C . This temperature dependence can be expressed by the equation (Arrhenius)

$$A = B \exp (-E/RT)$$

where A is the specific reaction rate changing with temperature, B is a constant, R the gas constant, T the absolute temperature and E an activation energy for the process of alkali removal from the glass. Alkali extraction is always associated with changes in pH and such changes depend upon the quantities of alkali and silica released.

Attack by Acid

Mineral acid The mode of attack is similar to that by water, namely at the site of the siloxane bond $\begin{array}{c} | \quad | \\ -\text{Si}-\text{O}-\text{Si}- \\ | \quad | \end{array}$. All silicates are massively attacked by hydrofluoric acid, although the form of the silica influences the reaction rate.



Hydrochloric and sulphuric acids are not so aggressive. Phosphoric acid when pure is no more corrosive than other mineral acids.

Organic acid Some glasses are more prone to attack by organic acids than by other acids with a lower pH value. These acids form complex ions in solution which increases the glass solubility. Many vitreous enamels contain lead oxide and are susceptible to attack by organic acids. Consequently their corrosion resistance is assessed by exposure to acetic or citric acids²¹. The test temperature is always stipulated because a rise of 10°C can double the rate of reaction between glass and acid.

Repairs to Enamel Damage

Repair cements are generally satisfactory and economical for mild chemical service and are effective over lengthy periods. For severe chemical service enamelled areas up to 120 mm in diameter can be repaired by specialists with metal plugs, tantalum discs and p.t.f.e. gaskets. These materials and glass have similar chemical resistance. Larger areas of damage or corrosion need special plates fixed with several studs and cement.

Complete re-enamelling of equipment is feasible, but this is often accompanied by distortion in the metal, and the process may in consequence be uneconomic.

Recent Developments

The traditional method of producing glass-lined vessels involves stages of annealing, degreasing, shot blasting, pickling, nickel 'flash' plating followed by application of up to two ground-coats and five cover-coats, each with a separate firing. Tighter legislation on waste-water treatment and higher energy costs are leading to the development of processes in which one or more of these stages may be omitted. These advances are achieved through greater understanding and control of glass composition, and by adopting more sophisticated powder handling techniques.

Glass Formulations

Glass frits used in vitreous enamels may contain as many as 20 components, though these may be classified into three functional categories. These are the glass formers, SiO_2 and B_2O_3 which constitute the random network of the glass, the dioxides, ZrO_2 which enhances alkali resistance and TiO_2 which is an opacifier, and the alkali and alkaline earths which lower fusion temperature and increase expansion coefficient. While high alkali content lowers resistance to acid attack, adequate amounts are required to dissolve the oxides on the surface of the steel. A relatively infusible ground-coat frit becomes supersaturated in iron oxide which eventually crystallises in the enamel, a defect known as 'copperheading'. Compromise is necessary, as too fluid a ground-coat results in over-rapid reaction and 'burning off'. Additions of alumina can be used to control viscosity.

Depending on the required chemical properties of the enamel, the appropriate area of the composition triangle (Fig. 18.5) is chosen.

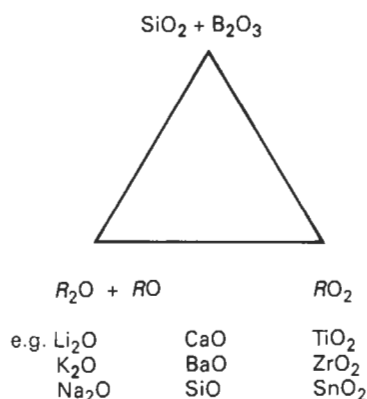


Fig. 18.5 Composition triangle for vitreous enamels

A high silica to boric oxide ratio composition is used in hot water tanks where the higher firing temperature is accepted for improved chemical and thermal resistance.

Opaque enamels contain up to 20% TiO_2 . These melt to a clear frit at 1400°C , then partially crystallise to anatase and rutile during the firing process at 800°C , giving excellent acid resistance and fairly good alkali resistance. Titania opacified frits are relatively hard, but viscous at the firing temperature, giving rise to porosity entrapment. Furthermore, the low expansion coefficient ($8-9 \times 10^{-6}$) may result in spontaneous chipping due to excessive compressive stresses generated at convex surfaces. Both problems are solved by adding lithia, making the glass more fusible and raising its expansion coefficient.

Crystalline Enamels

The glass ceramic process provides coatings that are harder and more wear resistant for the requirements of the chemical industry. Formulations are designed so that both fusion and crystallisation occur during a single firing schedule. Partridge²² describes glass ceramics based on the lithium aluminosilicate system (Li_2O (13.5%), K_2O (5.5%), B_2O_3 (0.8%), RO_2 (0.2%)) which have acceptable expansion coefficients and firing temperatures. They exhibit significantly higher strengths and better thermal shock resistance than glass ($>200^\circ\text{C}$ on quenched plate samples), but acid resistance is inferior. Corrosion rate is ~ 30 mpy using the thimble test in boiling 20% HCl compared with 3.1 mpy for a typical vitreous enamel. This is due to segregation of the vulnerable alkali ions into the minority glass phase of the material. For better corrosion resistance, a vitreous layer must be fired on as a top-coat.

Improved Processes

A number of commercial processes have been introduced in recent years which afford economic benefits

- (a) *ETE*: electrophoretic application which gives even build and thicker coating at convex surfaces.
- (b) *PUESTA*: powder electrostatic application dispenses with liquid spray or dip application, depositing the dry powder electrostatically.
- (c) *Direct-on*: modified enamel frits have been developed which can produce a good bond on steel without the previously required pickling and nickel-plating stages.
- (d) *Combismalt system*, or *two coat one fire*: the top-coat is applied on top of the dried ground-coat. To prevent mixing, larger quantities of deflocculent are added to the slurry of the base enamel. This results in a tighter binding of the particles so that the top-coat slurry does not penetrate the biscuit of the dried base. As well as the cost advantage due to fewer firings, thinner layers are produced which are less subject to chipping.

Corrosion Mechanisms

Studies on hot water tank enamels²³⁻²⁵ in media of varying pH demonstrate a minimum corrosion rate at pH value of 4. In citric acid (pH 2), IR measurements indicate that ion exchange is the principal mode of corrosion. Distilled water (pH 7) showed evidence of a bulk dissolution mechanism with no silica enrichment of the surface layer. In neutral solutions, the first stage of attack is leaching of alkali ions, raising the pH of solution, which subsequently breaks down the glass network of the acidic oxides.

Acid resistance is enhanced by fine milling and minimum clay additions to the slip. The setting agents (deflocculents) which hold the powder particles

in suspension are usually sodium compounds, and these tend to reduce the acid resistance. Alkali-free materials, such as benzoic or succinic acid, should be used for this purpose.

Enhanced anti-corrosion properties are also reportedly achieved by mill additions of lithium titanate, lithium aluminate or magnesium titanate to the host glass frit²⁶.

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C. A. MAY

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18.5 Stoneware

Introduction

Owing to their almost complete resistance to corrosion, stoneware and porcelain occupy a unique position as materials in the chemical industry. Stoneware bodies can be compounded from many different raw materials to give the properties required and to permit the manufacture of articles up to a considerable size. Porcelain, on the other hand, is not generally used for very large articles, but owing to its completely vitreous nature it normally shows a much greater resistance to corrosion than does stoneware.

The composition of stoneware can vary very widely. In its simplest form it may consist simply of a clay, or a clay mixed with a pre-fired inert material known as *grog*. This grog may be clay which has been fired to a high temperature and then crushed and sieved to give the correct grading. On the other hand, the body may be compounded from clays, felspar, quartz, etc. all materials which are in normal use in the ceramic industry. This type of body normally has improved strength over the simple type. The grog may be of a special nature, such as alumina, silicon carbide or zircon, according to the service conditions to which the material will be subjected in use. The appropriate type of body mix must be decided on in relation to materials which will be in contact with the ware, any thermal shock to which the ware may be subjected, and the mechanical forces the ware will have to withstand.

Mechanical and Physical Properties

While mechanical properties of ceramic materials are usually quite adequate for the duties which they have to perform, it is essential to realise the limitations of the material, and to design and install any articles made from it in such a way as to minimise any weakness. Table 18.12 gives typical values for the mechanical properties of the different materials which are available.

Tensile Strength

This depends very largely on the composition of the body and the temperature to which it is fired. The addition of a clay grog will normally reduce the tensile strength but the degree of reduction depends on the proportion used, the grain-size distribution of the grog, and the particle shape. The

Table 18.12 Some typical values for the physical and mechanical properties of available stoneware and porcelain bodies

Body	Property						
	Tensile strength (MN/m ²)	Com- pressive strength (MN/m ²)	Modulus of rupture (MN/m ²)	Apparent porosity (%)	Thermal conductivity (Wm ⁻¹ K ⁻¹)	Young's modulus (GN/m ²)	Thermal expansion coefficient 0-500°C (mm/mm°C)
Porcelain	34	690	90	0	0.0047	69	7×10^{-6}
Stoneware:							
Porous	7	103	34	0.5-0.3	0.0035	55	5×10^{-6}
Vitreous	21	207	70	0-0.5	0.0047	69	6×10^{-6}
Thermal- shock- resisting stoneware	14	138	55	0-1.0	0.0035	83	6×10^{-6}
High alumina	117	1 380	276	0	0.013	276	7×10^{-6}

degree of vitrification also affects the tensile strength. By using special grogs it is possible to produce a body which has a reasonably high strength.

Since all ceramic materials are weaker in tension than in compression, it is good practice in design to avoid tensile forces wherever possible, and where they are unavoidable to reduce them to a minimum and to distribute them evenly over the article, e.g. a circular tank is better than a rectangular one.

Compressive Strength

This is usually about ten times greater than the tensile strength and once again depends on the properties of the grog and the degree of vitrification of the body.

Modulus of Rupture

All ceramic materials are elastic, and hence show very little bending under load. They do not exhibit any creep under load. The modulus of rupture type of test¹ is the routine test most commonly used in the ceramic industry, and gives the figure generally quoted for the strength of the material. It must be remembered that the value obtained for any particular body depends on the cross-sectional area of the test piece; thus figures quoted from test results may be higher than those obtained on actual articles, which usually have a thicker section than the test piece.

Young's Modulus

This is normally very high and very little can be done by the manufacturer to vary it. An important related property is the critical strain, defined as the

ultimate tensile strength divided by the elasticity. Most ceramic materials have similar values for critical strain (approx. 0.001), and this must always be remembered whenever a combination of stoneware and other materials is being considered.

Porosity

This is very important as several other properties are dependent upon it. If the porosity is too high, the article will be weak and will not retain liquid. The pore structure should also be taken into account. When a ceramic material is fired, although the internal surface area decreases as the material approaches zero porosity, the mean radius of the pores increases. Thus, when the internal surface area is $3 \text{ m}^2/\text{g}$ the mean pore radius may be of the order of 10^{-7} m , while when the internal surface has dropped to $0.5 \text{ m}^2/\text{g}$ the mean pore radius may be about $4.5 \times 10^{-7} \text{ m}$. The mean pore radius may reach a value as high as $9 \times 10^{-7} \text{ m}$ as the ware approaches zero porosity during firing. It is thus obvious that at some point the pores must start to close up. This closing of the pores with the approach of vitrification is borne out by results of permeability measurements.

It is generally true that the lower the porosity the higher the mechanical strength and the acid resistance of the body, but unfortunately low porosity also usually results in reduced thermal shock resistance.

Thermal Shock Resistance

The thermal shock resistance of any stoneware material depends particularly upon thermal expansion, strength, Young's modulus and thermal conductivity.

Many of these properties depend upon others which may themselves be governed by yet other factors. Thus, as mentioned above, increased porosity usually gives better thermal shock resistance, but it may be necessary for reasons of watertightness to employ a body with a very low porosity. The size of an article is also closely related to the degree of thermal shock which it will withstand. For this reason it is very difficult to give accurate figures for the thermal shock resistance of stoneware bodies. In practice, if precautions are taken to heat up any stoneware articles slowly and evenly no trouble will be experienced. This is a matter on which the ceramic manufacturer should be consulted.

Dimensional Accuracy

All ceramic articles (except those for highly specialised uses) exhibit high shrinkage, usually varying between 7 and 15%, during manufacture. During the firing process the rate of shrinkage of different parts of an article may vary, and the body may slump under its own weight at the maximum temperature attained. Thus it can be seen that the manufacture of an article to a close dimensional specification is a very difficult task. Manufacturers

will normally contract to supply to dimensions with a tolerance of $\pm 2\%$. If greater accuracy than this is required, it is necessary to grind the article, which will increase the price.

Abrasion Resistance

This property is very hard to define, as articles may be subjected to very varied forms of abrasion, and in general a given ceramic body will react quite differently to different types of abrasion. This is a question on which the manufacturer should be able to give considerable guidance. Many types of standard abrasion test have been proposed, but none has proved satisfactory and experience must continue to be the main guiding factor.

Thermal Expansion

The thermal expansion coefficient of ceramic material can vary from 2×10^{-6} to 7×10^{-6} mm/mm°C. The values obtained for bodies normally supplied are about 5×10^{-6} to 6×10^{-6} mm/mm°C; values outside this range will be obtained only from special bodies.

Impact Strength

This is another property for which it is very difficult to obtain a reliable figure. In general, ceramic materials are not very resistant to impact and should be guarded to prevent breakage by accidental blows.

Chemical Resistance

Stoneware and porcelain are attacked only by hydrofluoric acid and hot concentrated caustic alkalis and are almost completely unaffected by all concentrations of mineral and organic acids, acid salts and weak alkalis². The degree of susceptibility depends upon composition, firing temperature and porosity.

As stoneware and porcelain can be given a glazed finish on both interior and exterior surfaces, articles made from these materials can be very easily cleaned, even after years of use. The glaze also has an effect on the strength of the ware, increasing it by up to 20%, but certain types of body are difficult to glaze satisfactorily.

Jointing

In the majority of stoneware constructions some form of joint has to be provided, and in runs of piping there will be very many joints, which frequently fail owing to failures in the jointing material. It is essential that all

joints should be able to withstand corrosion to the same extent as the stoneware, and that they should be leakproof and capable of withstanding any conditions of mechanical or thermal shock which may be present. For these reasons, very careful thought must be given to the type of joint employed and to the jointing media. It should also be remembered that any joints should be made by skilled operatives, as in most cases one badly made joint could cause failure of the whole installation.

Various methods of jointing are discussed below.

Hydraulic Cement

Three types of hydraulic cement are in use, viz. Portland, supersulphated and high-alumina. Portland cement is satisfactory in solutions with a pH of 7 and upwards, high-alumina will withstand solutions of pH 5.5 and upwards but will be attacked by alkaline solutions greater than pH 9, while supersulphated cement is resistant to solutions of pH 3 and upwards and also to alkaline solutions. All these cements are resistant to solvent solutions. Another advantage in the use of high-alumina cements is that they will attain their maximum strength in about 24 h. If Portland cement is used for the foundations of acid plants, care should be taken to insulate it from the surrounding earth.

Acid-resisting Cement

This class of cement, which will withstand acids of all concentrations, with the exception of hydrofluoric acid, consists of an inert aggregate bonded with either potassium or sodium silicate solution, with the addition of a setting agent, e.g. sodium silicofluoride or ethyl acetate. The aggregate may consist of graded quartz, acid-resisting brick, etc. It is important to remember that this type of cement will be attacked by water and dilute alkalis, and therefore an acid solution must be kept in contact with the cement during use. Sodium silicate is the normal bond used, mainly on account of its cheapness. In the presence of sulphuric acid, however, potassium silicate is preferable, since if sodium silicate is used, there is a danger that the decahydrate of sodium sulphate will be formed, with a consequent large increase in volume. Many trials of the use of sodium silicate in contact with sulphuric acid have however shown very little evidence that this disintegration will actually take place.

Rubber Latex and Resin Cements

Rubber latex cement Rubber latex cement consists of mixtures of sand and other fillers which are gauged with rubber latex solution. These cements are suitable for dilute acid conditions and are particularly useful in conditions where dilute acid alternates with water or dilute alkalis. They remain very slightly resilient and adhere very well to stoneware. They are not of course

resistant to organic solvents which would normally attack rubber, nor to strongly oxidising acid solutions which cause ageing of the rubber.

Resin cements Many different resin cements are now available, and types which give satisfactory service under most conditions can be obtained³.

Many formulae have been suggested for cement using sulphur, e.g. sulphur and sand, sulphur bitumen and sand, etc. These materials are heated in a vat until molten and then poured into the joints where they set to a hard, strong solid. They are usually very brittle and contract considerably on cooling, which may give rise to cracks. They are, however, resistant to acid, water and dilute alkalis.

Lutes

This class of material does not set and must be held in position by a rigid cement or some mechanical means. A material commonly used is asbestos fibre mixed with various other substances such as china clay, sand, etc. and plasticised with some form of oil or tar.

Fixed-flange Piping

In this method of jointing stoneware piping, the joint is formed by a gasket between ground ends of the pipe, the joint being put under compression by a metal clamp. The choice of gasket material will of course depend upon service conditions.

Rubber Sleeves

This is a fairly modern development in which the joint is formed from a rubber sleeve which rolls along the pipe as it is pushed into the spigot of the next pipe, to form a very strong joint, which is highly resistant to vibration*.

Chief Applications

Stoneware is used mainly for storage, transportation and processing, where its great resistance to corrosion is important. As it can be glazed and is completely non-reactive, it is also used in situations where cleanliness is important, as in the food industry.

Storage vessels can be made in a large variety of shapes and sizes. Absorption and distillation towers are available in several different forms and many sizes. Reaction vessels such as coppers, stills and Cellarius receivers can be supplied in the special materials to withstand thermal shock. Valves and pumps of many types are available to suit all conditions. Piping can be

* Flexadrain Joint, developed by the National Salt Glazed Pipe Man. Assn. and British Ceramic Research Assn.

supplied in a great number of bore sizes, complete with the necessary bends, and with any desired form of joint.

Porous articles for filtration, aeration, diffusion, etc. can also be made from materials having the same chemical inertness as those used for the low-porosity articles such as storage vessels. The pore size of these articles can be controlled to suit the operating conditions encountered.

Costs

Costs of stoneware articles are usually lower than those of competitive materials. The cost per pound is always much lower, but the degree of complexity of the required article and its availability or otherwise in standard stock sizes will, of course, influence the total cost. Owing to the manufacturing methods employed for stoneware, special designs may easily be produced, and hence mould charges may be very low.

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18.6 Plastics and Reinforced Plastics

For very many years organic materials have been used for coating metals to protect them against corrosion. During the present century two complementary trends may clearly be discerned. The first is the progressive replacement of natural materials with synthetic materials of high molecular weight belonging to a chemical class referred to as *polymers*. The second is the increased use of these materials, not simply as a protective coating for some material of construction, but as a material of construction itself. Thus such materials have extended from two-dimensional applications as surface coatings to three-dimensional forms, which are referred to as *plastics*.

Hence whilst in the past corrosion control has involved, in the main, the use of metal alloys, protective coatings, inhibitors, etc. corrosion problems may now often be circumvented by the use of self-supporting organic polymers in the form of either rubbers or plastics. It must however be immediately stressed that such materials are not invariably inert to chemicals and they display their own particular response to such materials. A consideration of such behaviour will be a prior object of this section.

Definition of 'Plastics'

It is in fact exceedingly difficult to provide a satisfactory definition of the term *plastics*, since attempts at reasonably concise definitions tend to include certain materials such as rubbers, adhesives, fibres, glasses and surface coatings that are not usually considered as plastics, and to exclude a number of somewhat non-typical materials such as bituminous plastics, shellac and polytetrafluorethylene which usually are. In reality then, the term becomes bounded by common usage rather than by a physical-chemical description. However, in general, it may be said that plastics are usually high polymers that at some stage in their existence are capable of flow, but may also be brought into a non-fluid form in which they have sufficient toughness and strength to be useful in self-supporting applications. Although they may be self-supporting this does not exclude the possibility of reinforcing the plastics with fibres or of laminating them with other materials. Sometimes metals are coated with plastics but usually at a greater thickness than is common with traditional surface coatings such as paint films. (See Section 16.2.)

The rapid rise of the plastics industry since World War II may be attributed to a number of factors. Foremost has been the fact that whilst many materials of construction have been subjected to continual increases in their price, the development of the petrochemicals industry and economies of scale have, for most of the time, led to reductions in the prices of plastics materials. With the passage of time more and more products constructed from traditional materials have become cheaper to produce from plastics. Whilst economies of scale have probably almost reached their limits, and whilst the low profitability of many plastics-producing plants may cause companies to retard increases in plant and production, the trend of increased plastics usage seems bound to continue.

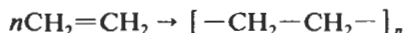
Such an increase also requires that plastics possess properties suitable for the end-use envisaged. Whilst it is today possible, by chemical modification or the selective use of additives, to make products varying widely in their properties, certain properties are common to the vast bulk of plastics materials. These include:

1. Tenacity. Whilst some plastics are rigid and others flexible, all commercial materials show a degree of strength and toughness superior to simple crystals and common glass when rapidly stressed.
2. Low thermal conductivity.
3. Low electrical conductivity.
4. Low heat resistance compared with common metals. The vast bulk of plastics produced will not withstand 100°C and only a very few highly specialised products will withstand 400°C.

The Chemical Nature of Plastics

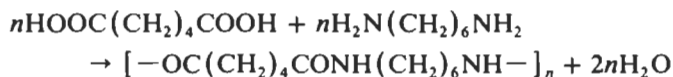
Most plastics are based on polymers, which may be prepared by a variety of techniques that are briefly as follows.

Double-bond polymerisation In this case the double bond in a small molecule opens up and allows it to join to another similar molecule, e.g. with ethylene:



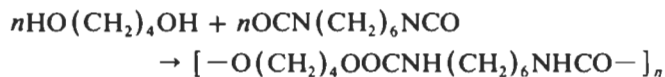
The molecules join together to form a long chain-like molecule which may contain many thousands of ethylene units. Such a molecule is referred to as a *polymer*, in this case polyethylene, whilst in this context ethylene is referred to as a *monomer*. Styrene, propylene, vinyl chloride, vinyl acetate and methyl methacrylate are other examples of monomers which can polymerise in this way. Sometimes two monomers may be reacted together so that residues of both are to be found in the same chain. Such materials are known as *copolymers* and are exemplified by ethylene-vinyl acetate copolymers and styrene-acrylonitrile copolymers.

Condensation polymerisation In this case reaction between two groups occurs which leads to the production of a polymer and also a simple molecule, e.g. reaction between adipic acid and hexamethylene diamine yields nylon 66 and water:

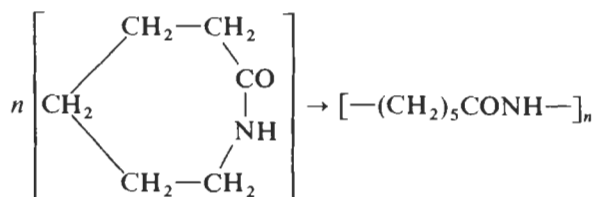


Most nylons, polyesters, phenolics and a number of other plastics are produced by this route.

Rearrangement polymerisation Here the mechanism resembles condensation polymerisation but no small molecule is split out. In the first example, 1:4-butane diol reacts with hexamethylene di-isocyanate to give 6,4-polyurethane:



In the second, ϵ -caprolactam, a ring compound, opens up to give nylon 6:



The polymerisation of ϵ -caprolactam is sometimes known as a *ring-opening* polymerisation, a technique also used with ethylene oxide, tetrahydrofuran and a number of other monomers.

Polymers may also be obtained from another source—nature. Cellulose, the principal constituent of cotton and a major constituent of wood, is a polymer. So also are lignin, natural rubber, gutta percha and proteins. Sand (silica) may be considered as an inorganic polymer. Whilst many of these are of value unmodified, some, like cellulose, cannot be considered as plastics in their natural state, but if chemically modified by man useful plastics materials such as cellulose acetate, celluloid and ethyl cellulose may be obtained.

The Physical Nature of Plastics

Many polymers such as polystyrene consist of long chain-like molecules of very high molecular weight. A typical molecular weight for a polystyrene molecule is about 200 000, and since the molecular weight of the monomer is 104 there may well be 2 000 monomer units joined together in this way. Since the backbone carbon-carbon bonds can rotate freely, such molecules are most unlikely to be stretched out in straight lines but are more likely to be coiled up into a random configuration.

In the case of polystyrene the molecules at room temperature do not have enough energy to twist and move around and so in the mass the polymer is rigid. On heating above a certain temperature range sufficient energy for movement is obtained and on application of a shearing stress the polymer molecules partly uncoil, slip past each other and, in the mass, flow occurs. On cessation of stress, slippage ceases, the chains again coil up and

on cooling the mass again hardens. If desired, the whole process of heating, shearing and cooling may be repeated and materials which behave in this way are known as *thermoplastics*. Two points should, however, be noted. Firstly, if cooling precedes chain recoiling then a frozen-in molecular orientation will result which can grossly affect the polymer properties, in some cases adversely. Secondly, repeated heating and shearing may be accompanied by changes such as oxidation and polymer degradation which will limit in practice the number of times heating and cooling can be undertaken on a particular polymer sample.

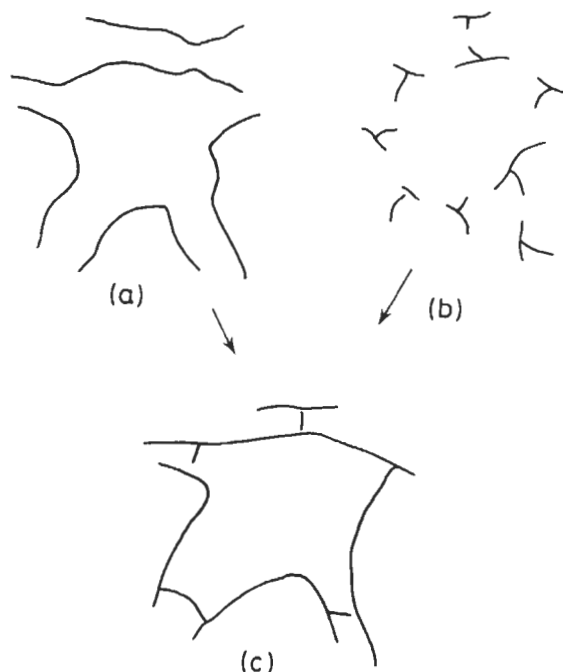


Fig. 18.6 Joining up of (a) long-chain molecules or (b) branched molecules to produce (c) a cross-linked polymer

In terms of tonnage the bulk of plastics produced are thermoplastics, a group which includes polyethylene, polyvinyl chloride (p.v.c.), the nylons, polycarbonates and cellulose acetate. There is however a second class of materials, the thermosetting plastics. They are supplied by the manufacturer either as long-chain molecules, similar to a typical thermoplastic molecule or as rather small branched molecules. They are shaped and then subjected to either heat or chemical reaction, or both, in such a way that the molecules link one with another to form a *cross-linked network* (Fig. 18.6). As the molecules are now interconnected they can no longer slide extensively one past the other and the material has *set*, *cured* or *cross linked*. Plastics materials behaving in this way are spoken of as *thermosetting* plastics, a term which is now used to include those materials which can in fact cross link with suitable catalysts at room temperature.

Important thermosetting plastics include the phenolics, melamine-formaldehyde, epoxides and polyester resins used in glass-reinforced plastics. (See also Sections 14.5 and 14.9.)

Thermoplastics

Thermoplastics may themselves be considered in four sub-classes: (a) amorphous thermoplastics, (b) rubber-modified amorphous thermoplastics, (c) plasticised amorphous thermoplastics and (d) crystalline thermoplastics.

Amorphous thermoplastics These are made from polymers which have a sufficiently irregular molecular structure to prevent them from crystallising in any way. Examples of such materials are polystyrene, polymethyl methacrylate and polyvinyl chloride.

At very low temperatures these materials are glass-like and rigid. On heating, a temperature is eventually reached when the material softens. If the polymer is of sufficiently high molecular weight it does not melt but becomes rubbery. The temperature at which this occurs is known as the glass transition (T_g), and is in effect the point at which the molecules have sufficient energy to be able to coil and uncoil; however, chain entanglements prevent flow. At higher temperatures there are two possibilities. Polymers of moderate molecular weight may achieve such energy that they can flow, whilst high molecular weight materials may decompose before the flow point is reached. This is shown schematically in Fig. 18.7 which indicates the phases in which this type of polymer can occur. It should be stressed that the boundary lines will change position with change of polymer species.

It will be seen that a polymer of molecular weight M_1 may be processed either as a liquid (by injection moulding, extruding, etc.) or as a rubber (by vacuum forming, sheet blowing, warm forging). In the case of the polymer

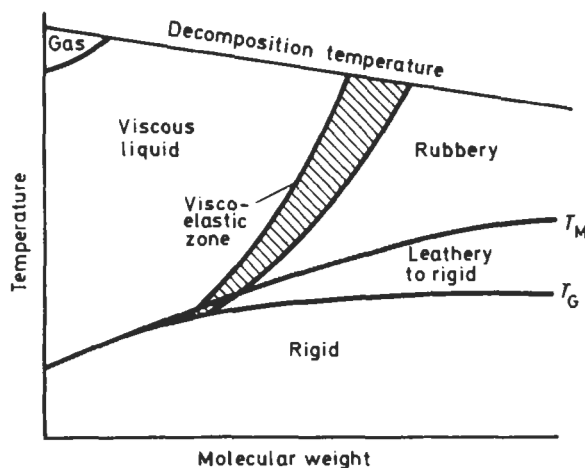


Fig. 18.7 Temperature-molecular weight phase diagram for amorphous polymers

of molecular weight M_2 it will be seen that it can only be shaped in the rubbery state, and if it is intended to process it by say injection moulding then the molecular weight will first have to be reduced. An important illustration of this is with the well known acrylic materials such as Perspex and Oroglas which have too high a molecular weight to be injection moulded. However, lower molecular weight polymers (e.g. of molecular weight M_1 in Fig. 18.7) of similar chemical structure are available (e.g. Diakon) which are suitable for this purpose.

It is possible to make some generalisations about the properties of amorphous thermoplastics:

1. The T_g will determine the maximum temperature of use of the material as a rigid thermoplastic. For amorphous rubbers the T_g will determine the minimum temperature.
2. Below T_g most amorphous polymers show a more or less linear stress-strain curve with no yield point (Fig. 18.8)

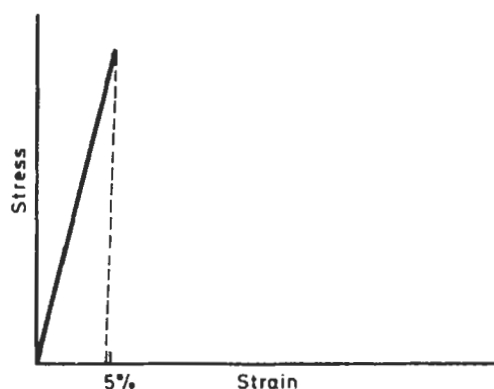


Fig. 18.8 Typical stress-strain curve of amorphous thermoplastics below their glass transition temperature. Area under the curve is small compared with many crystalline plastics and hence the impact strength is usually low

The tensile strengths are about 55 MN/m^2 , the elongations at break usually less than 10% and the modulus of elasticity about 2.7 GN/m^2 . Since the area under the curve provides a measure of the energy required to break the bonds, and since this area is small such polymers will have a low impact strength (which is closely related to energy to break) and will break with a brittle fracture.

3. They are generally more permeable to gases than crystalline polymers, more so above T_g than below (see later).
4. They usually have a much wider range of solvents than crystalline polymers (see later).

Rubber-modified amorphous polymers The brittleness of amorphous polymers has been a hindrance in their commercial development. Fortunately, for reasons still not fully understood, the addition of rubbery polymers as dispersed droplets, or sometimes in a network form, into the glassy polymer can often lead to substantial increases in impact strength, albeit usually at

some cost to tensile strength and, in many cases, clarity. Such materials still, however, have a phase diagram similar to Fig. 18.7 except that the terms 'glassy' and 'glass-transition' temperature are no longer strictly accurate.

The most important polymers of this important class are:

1. High-impact polystyrene (polystyrene modified with styrene-butadiene rubber (SBR) or polybutadiene rubber).
2. ABS—A complex polymer based on acrylonitrile, butadiene and styrene.
3. Methacrylate-butadiene-styrene polymers (MBS) and related materials chemically similar to ABS but often available in transparent form.
4. High-impact p.v.c.—in this case the impact modifiers are not always rubbers but the mechanism of their action is probably similar.

Plasticised amorphous thermoplastics Certain plastics may be mixed with high-boiling low-volatility liquids to give products of lower T_g . The most important example occurs with p.v.c. which is often mixed with liquids such as di-iso-octyl phthalate, tritolyl phosphate or other diesters to bring the T_g below room temperature. The resultant plasticised p.v.c. is flexible and to some degree quite rubbery. Other commonly plasticised materials are cellulose acetate and cellulose nitrate.

It is essential to appreciate that such plasticisers will considerably modify the chemical properties of the plastics material since the plasticiser may be readily extracted by certain chemicals and chemically attacked by others whilst the base polymer may be unaffected.

Crystalline thermoplastics Whilst polymers such as polyethylene and nylon 66 do not show any regular external form which is characteristic of crystals, closer examination reveals that they have many properties common to crystalline materials. Although the exact nature of this crystallinity is still a matter of dispute it would appear that segments of polymer molecules at least pass through zones in which molecular arrangement is highly ordered, i.e. crystalline. In some ways these zones act like knots or cross-links holding the materials together.

The effect of heating crystalline polymers from low temperatures is more complex than with amorphous polymers. Initially the material is rigid and hard. As the temperature goes through the T_g , lightly crystalline material softens slightly and becomes leatherlike, but highly crystalline materials show little change in properties. Further heating results in the crystals melting over a temperature range and the polymer becomes rubbery. Whether or not it melts or decomposes first on further increases in temperature will depend on molecular weight as with amorphous polymers.

A typical phase diagram for such polymers is given in Fig. 18.9. With such crystalline polymers the melting point T_m replaces the T_g as the factor usually determining the maximum service temperature of thermoplastics and minimum service temperature of rubbers. However, being more complicated than amorphous polymers it is more difficult to make generalisations about properties. The following remarks may, however, be pertinent for crystalline polymers:

1. Below T_g tensile strengths are usually at least as strong for crystalline polymers as for amorphous polymers. Between T_m and T_g the strength and rigidity will be very dependent on the degree of crystallinity and

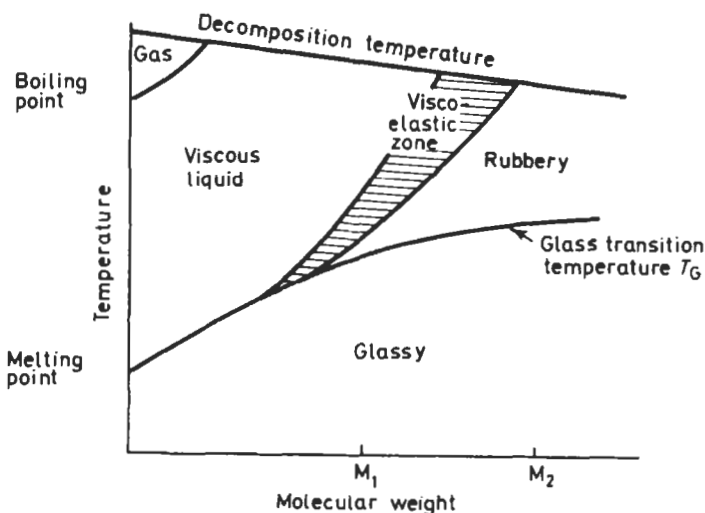


Fig. 18.9 Temperature-molecular weight phase diagram for crystalline polymers

to some extent on molecular weight, e.g. tensile strengths can range from 7 to 84 MPa².

2. In most cases crystal densities differ from the densities of amorphous polymers. This leads to differences in refractive index, which in turn cause scatter of light at boundaries between amorphous and crystalline zones. Such materials are opaque except in certain instances where the crystal structure can be carefully oriented to prevent such scatter of light.
3. The close molecular packing makes diffusion more difficult than with amorphous polymers compared in similar circumstances, i.e. both below T_g or both above T_g (but below T_m of the crystalline polymer).
4. Thermodynamic considerations lead to considerable restriction in the range of solvents available for such polymers.

Thermosetting Plastics

If glycerol is reacted with phthalic anhydride three ester links can be made from each glycerol unit. Continued reaction will eventually cause the molecules to link up in a three-dimensional network in which, theoretically at least, the whole polymer mass becomes one giant molecule.

For reasons of production feasibility such cross-linked plastics are normally prepared in two stages. In the first stage either a low molecular weight branched polymer or a higher molecular weight linear (unbranched) polymer is produced. Such materials are thermoplastic and in most cases soluble in appropriate solvents. By activation of heat and/or additional chemical reactants, the branched molecules join together, or the linear polymers cross link, to produce an infusible, insoluble material. Since, in the early days of the plastics industry, the cross-linking processes required heat these materials became known as *thermosetting* plastics. Today this term is commonly extended to materials which can cross link at room temperature.

Because thermosetting plastics have an irregular form they are amorphous and because of the network structure are invariably rigid. They do not dissolve without decomposition but may swell in appropriate solvents, the amount of swelling decreasing with increased cross-link density.

Well-known thermosetting plastics include the phenolics, urea-formaldehyde and melamine-formaldehyde plastics, polyesters and epoxides.

Reinforced Plastics

The mechanical properties of plastics materials may often be considerably enhanced by embedding fibrous materials in the polymer matrix. Whilst such techniques have been applied to thermoplastics the greatest developments have taken place with the thermosetting plastics. The most common reinforcing materials are glass and cotton fibres but many other materials ranging from paper to carbon fibre are used. The fibres normally have moduli of elasticity substantially greater than shown by the resin so that under tensile stress much of the load is borne by the fibre. The modulus of the composite is intermediate to that of the fibre and that of the resin.

In addition to the nature of resin and fibre, the laminate properties also depend on the degree of bonding between the two main components and the presence of other additives including air bubbles. Because of this some parts, fabricated by simple hand building techniques, may exhibit strengths no better or even worse than unreinforced materials. This problem is often worst with glass fibres which are therefore normally treated with special finishes to improve the resin-glass bond.

The highest mechanical strengths are usually obtained when the fibre is used in fine fabric form but for many purposes the fibres may be used in mat form, particularly glass fibre. The chemical properties of the laminates are largely determined by the nature of the polymer but capillary attraction along the fibre-resin interface can occur when some of these interfaces are exposed at a laminate surface. In such circumstances the resistance of both reinforcement and matrix must be considered when assessing the suitability of a laminate for use in chemical plant. Glass fibres are most commonly used for chemical plant, in conjunction with phenolic resins, and the latter with furane, epoxide and, sometimes, polyester resins.

Polymer Orientation

It is not very difficult to appreciate that if polymer molecules are aligned as in Fig. 18.10 then a much higher tensile strength will be obtained if a test is carried out in the X-X direction as opposed to the Y-Y direction. It is also not difficult to understand why such a material has a lower impact strength than a randomly coiled mass of molecules (Fig. 18.10) because of the ease of cleavage of the material parallel to the X-X direction.

Similar remarks may also be made where crystal structures or fibre reinforcements rather than the individual molecules are aligned.

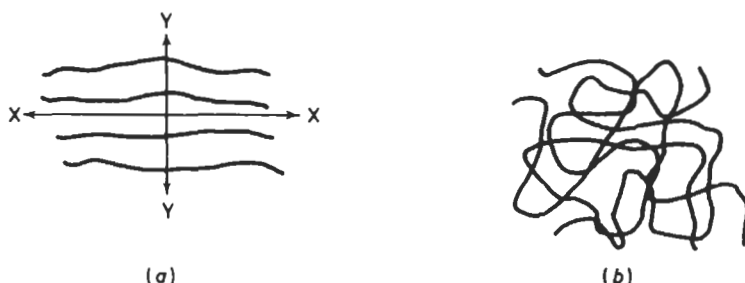


Fig. 18.10 Polymer alignment. (a) Parallel and (b) random

For fibres and filaments such orientation is desirable, but for solid objects where impact strength is often more important than tensile strength such orientation is usually unwelcome. It can also have further unwanted effects. This arises from the fact that oriented molecules are basically unstable and will at the first opportunity try to coil up. Thus on heating samples up to temperatures near T_g severe distortion can occur leading to warped mouldings.

Another serious effect occurs with liquids which are not in themselves solvents but which may wet the polymer surfaces. These facilitate relief of frozen-in stresses by surface cracking which can be a severe problem in using many injection and blow mouldings with specific chemicals. Examples of this are white spirit with polystyrene, carbon tetrachloride with polycarbonates and soaps and silicone oils with low molecular weight polyethylenes.

In addition to orientation in one direction (mono-axial orientation), biaxial orientation is possible. This is achieved when sheet is stretched in two directions resulting in layering of the molecules. This can increase the impact strength, tensile strength and solvent cracking resistance of polymers and with crystalline plastics the polymer clarity may also be improved.

To summarise this section let it be said that it is necessary for the technologist to control orientation, not the least because of the effect that this might have on stress-cracking that may occur in aggressive chemical environments.

The Chemical Properties of Polymers

It is common practice to talk about the chemical resistance of polymers without it always being appreciated that this can mean different things. To avoid this it is probably wiser to differentiate between:

1. Resistance of a polymer to chemical attack resulting in breakdown of some covalent bonds and formation of new ones. This could involve breakdown initiated by heat and radiation including u.v. light.
2. Resistance to dissolution by liquids.
3. Resistance to cracking in aggressive environments.
4. Permeability to gases and liquids.

It is also important to bear in mind that, for end use, polymers may be mixed with a number of additives such as plasticisers, stabilisers, anti-oxidants, fillers, fire-retardants, pigments and so on, and that this may well

have an important influence on chemical properties. The following discussion will however confine itself to pure polymers.

Resistance to Chemical Attack

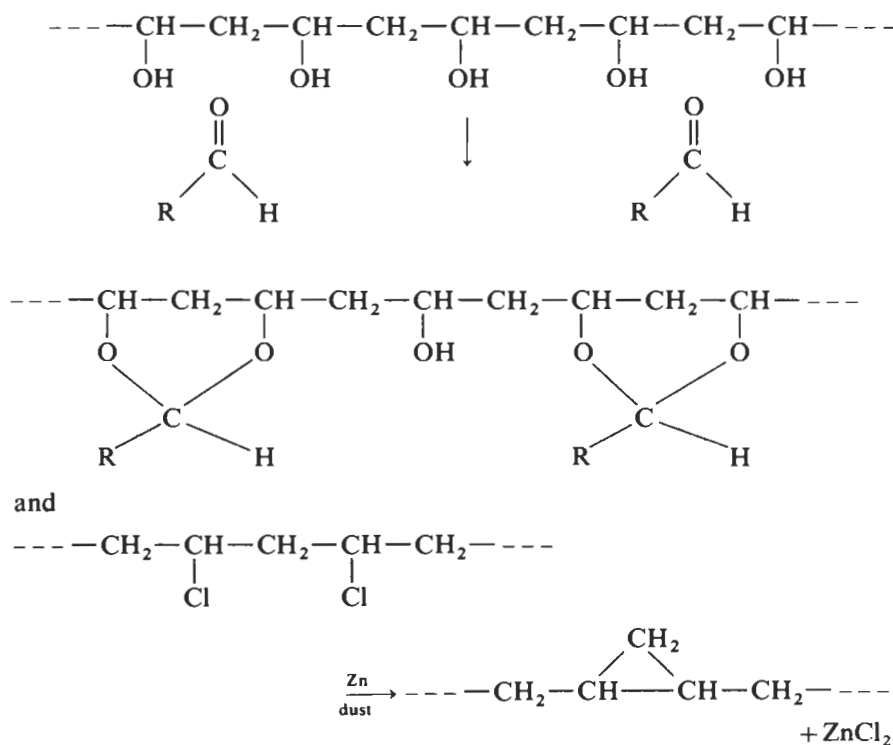
Expressed simply the resistance of a polymer to chemical attack may be said to be determined by the following factors:

- (a) Nature of the chemical bonds present.
- (b) Interaction between chemical groups which occur repeatedly along the molecular chain.
- (c) Presence of occasional 'weak-links'.

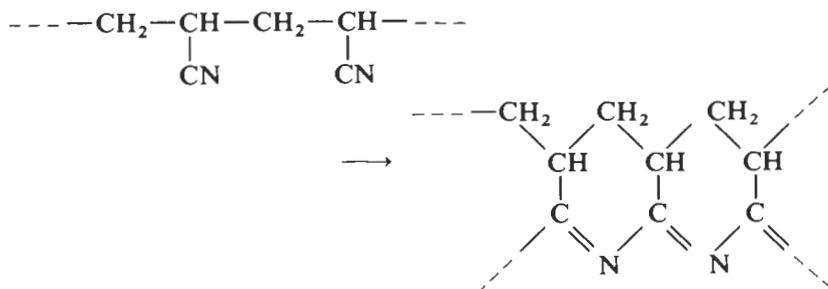
In commercial polymers there are a rather limited number of chemical bonds to be found and it is possible to make a number of general observations about the chemical reactivity in the following tabulated list of examples¹:

1. Polyolefins such as polyethylene and polypropylene contain only C—C and C—H bonds and may be considered as high molecular weight paraffins. Like the simpler paraffins they are somewhat inert and their major chemical reaction is substitution, e.g. halogenation. In addition, the branched polyethylenes and all the higher polyolefins contain tertiary carbon atoms which are reactive sites for oxidation. Because of this it is necessary to add antioxidants to stabilise the polymers against oxidation. Some polyolefins may be cross linked by peroxides.
2. Polytetrafluoroethylene contains only C—C and C—F bonds. These are both very stable and the polymer is exceptionally inert. A number of other fluorine-containing polymers are available which may contain in addition C—H and C—Cl bonds. These are somewhat more reactive, and those containing C—H bonds may be cross linked by peroxides and certain diamines and di-isocyanates.
3. Many polymers, such as the diene rubbers, contain double bonds. These will react with many agents such as oxygen, ozone, hydrogen halides and halogens. Ozone, and in some instances oxygen, will lead to scission of the main chain at the site of the double bond and this will have a catastrophic effect on the molecular weight. The rupture of one such bond per chain will halve the average molecular weight.
4. Ester, amide and carbonate groups are susceptible to hydrolysis. When such groups are found in the main chain, their hydrolysis will also result in a reduction of molecular weight. Where hydrolysis occurs in a side chain the effect on molecular weight is usually insignificant. The presence of benzene rings adjacent to these groups may offer some protection against hydrolysis except where organophilic hydrolysing agents are employed.
5. Hydroxyl groups are extremely reactive. These occur attached to the backbone of the cellulose molecule and polyvinyl alcohol.
6. Benzene rings in both the skeleton structure and on the side groups can be subjected to substitution reactions. Such reactions do not normally cause great changes in the fundamental nature of the polymer, e.g. they seldom lead to chain scission or cross linking. (N.B. The phenolic resins provide an important exception here.)

There are numerous examples of chemical reactions consequent upon chemical groups which occur repeatedly along a chain. In some cases the reaction occurs randomly between adjacent pairs of groups such as in the reaction between aldehydes and polyvinyl alcohol and of zinc dust with polyvinyl chloride:



In other instances the reactions appear to occur in sequence down the chain, for example in the depolymerisation reaction of polyformaldehyde (polyacetal) and polymethyl methacrylate which are referred to as *zippering* or sometimes *unzippering* reactions. In other cases cyclisation reactions can occur such as on heating polyacrylonitrile:



It is commonly found that polymers are less stable particularly to molecular breakdown at elevated temperatures than low molecular weight materials containing similar groupings. In part this may be due to the constant repetition of groups along a chain as discussed above, but more frequently it is due to the presence of weak links along the chain. These may be at the end of the chain (terminal) arising from specific mechanisms of chain initiation and/or termination, or non-terminal and due to such factors as impurities which becomes built into the chain, a momentary aberration in the *modus operandi* of the polymerisation process, or perhaps, to branch points.

The combination of weak links and unzipping can be catastrophic and has been a particular problem in the commercial development of some polymers, in particular polyacetals.

Polymer Solubility

The solution properties of polymers have been subjected to intensive study, in particular to highly complex mathematical treatment^{2,3}. This section will, however, confine discussion to a qualitative and practical level^{1,6}.

One chemical will be a solvent for another if the molecules are able to co-exist on a molecular scale, i.e. the molecules show no tendency to separate. In these circumstances we say that the two species are *compatible*. The definition concerns equilibrium properties and gives no indication of the rate of solution which will depend on other factors such as temperature, the molecular size of the solvent and the size of voids in the solute.

Molecules of two different species will be able to co-exist if the force of attraction between different molecules is not less than the forces of attraction between two like molecules of either species. This is shown more clearly by reference to Fig. 18.11 which shows two types of molecules, *A* and *B*. The average forces between the like molecules are F_{AA} and F_{BB} , and the average forces between dissimilar molecules are F_{AB} . If F_{AA} was the largest of these three forces then the *A* molecules would tend to congregate or cohere, pushing away the *B* molecules. A similar phase separation would occur if F_{BB} was the greatest.

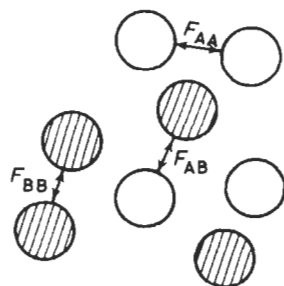


Fig. 18.11 Two different molecular species will be compatible if $F_{AB} \geq F_{AA}$ and $F_{AB} \geq F_{BB}$. In other circumstances the molecules will tend to separate if they have sufficient energy for molecular movement

It is therefore seen that only when

$$F_{AB} \geq F_{AA} \quad \dots (18.6)$$

and

$$F_{AB} \geq F_{BB} \quad \dots (18.7)$$

will co-existence or compatibility be possible. Obviously if it is possible to obtain some measure of these forces it should be possible to make predictions about polymer solubility. What then is a suitable measure of the forces holding like molecules together? One would expect the latent heat of vaporisation L to exceed that cohesion energy by an amount corresponding to the mechanical work done by evaporation, an amount approximating to RT where R is the gas constant and T the absolute temperature. Such a figure of $(L - RT)$ might be a sufficient measure if all of the molecules were of about the same size.

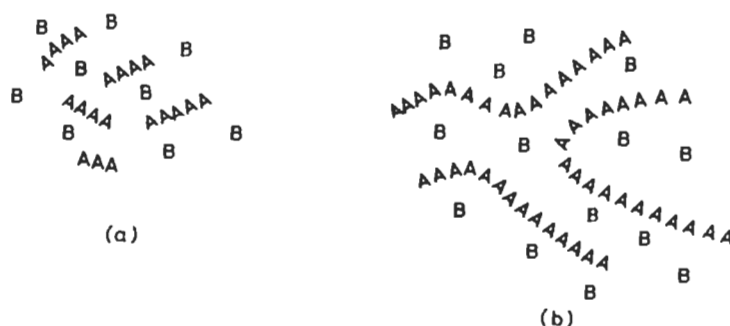


Fig. 18.12 Polymer molecules. (a) Short and (b) long

However, it is reasonable to suppose that compatibility should not be greatly affected by molecular size and that the shorter polymer molecules in Fig. 18.12 should be just as compatible as the longer molecules in Fig. 18.12b, although their latent heats of vaporisation will be greatly different. In such circumstances a reduced figure of $(L - RT)/M$ will give a measure of intermolecular energy per unit weight. Similarly, a measure of the intermolecular or cohesion energy per unit volume will be given by the expression:

$$\frac{L - RT}{M/D}$$

This expression is known as the *cohesive energy density* and in S.I. is expressed in units of megapascals. The square root of this expression is more commonly encountered in quantitative studies and is known as the *solubility parameter* and given the symbol δ , i.e.:

$$\delta = \sqrt{\frac{L - RT}{M/D}} \text{ MPa}^{\frac{1}{2}}$$

The solubility parameter is thus an experimentally determinable property, at least for low molecular weight materials, and a number of methods have been reviewed by Burrell⁴. In the case of polymers which cannot normally

be vaporised without decomposition, a method of calculating from a knowledge of structural formula has been devised by Small⁵. An excellent review of the whole subject is given by Gardon⁶.

It is now possible to provide an estimate of F_{AA} and F_{BB} , but the magnitude of F_{AB} will have to be considered separately for different systems.

Amorphous non-polar polymers and amorphous non-polar solvents It is assumed in these circumstances, by analogy with gravitational and electrostatic attraction, that F_{AB} will be equal to the geometric mean of F_{AA} and F_{BB} . If by definition we take $F_{AA} > F_{BB}$ then:

$$F_{AA} > F_{AB} > F_{BB} \quad \dots (18.8)$$

If we now consider the inequalities given in equations 18.6 to 18.8 it will be seen that compatibility can only occur between amorphous non-polar polymers and solvents when:

$$F_{AA} = F_{AB} = F_{BB}$$

i.e. when polymer and solvent have similar solubility parameters (in practice within about 2 MPa^{1/2}).

Reference to the values of δ in Tables 18.13 and 18.14 provides a number of examples of this. For example, natural rubber (unvulcanised) ($\delta = 16.5$) is dissolved by toluene ($\delta = 18.2$) and carbon tetrachloride ($\delta = 17.5$), but not ethanol ($\delta = 25.9$). Cellulose diacetate ($\delta = 23.2$) is soluble in acetone ($\delta = 20.4$), but not methanol ($\delta = 29.6$) or toluene ($\delta = 18.2$).

It should be noted that apart from the problem of achieving a molecular level of dispersion it is not necessary for the solvent to be liquid—it may be an amorphous solid.

Such tables are of greatest use with non-polar materials with values of δ not exceeding 19.4 and when the polymers are amorphous. It is now necessary to consider other systems.

Table 18.13 Solubility parameters of polymers

<i>Polymer</i>	δ MPa ^{1/2}	<i>Polymer</i>	δ MPa ^{1/2}
Polytetrafluorethylene	12.6	Polyethyl acrylate	18.8
Polychlorotrifluorethylene	14.7	Polysulphide rubber	18.4–19.2
Polydimethyl siloxane	14.9	Polystyrene	18.8
Ethylene-propylene rubber	16.1	Polychloroprene rubber	18.8–19.2
Polyisobutylene	16.1	Polymethyl methacrylate	18.8
Polyethylene	16.3	Polyvinyl acetate	19.2
Polypropylene	16.3	Polyvinyl chloride	19.4
Polyisoprene (natural rubber)	16.5	Bisphenol A polycarbonate	19.4
Polybutadiene	17.1	Polyvinylidene chloride	20.0–24.9
Styrene-butadiene rubber	17.1	Ethylcellulose	17.3–21.0
Poly- <i>t</i> -butyl methacrylate	16.9	Cellulose dinitrate	21.5
Poly- <i>n</i> -hexyl methacrylate	17.5	Polyethylene terephthalate	21.8
Poly- <i>n</i> -butyl methacrylate	17.7	Acetal resins	22.6
Polybutyl acrylate	18.0	Cellulose diacetate	23.1
Polyethyl methacrylate	18.4	Nylon 66	27.7
Polymethylphenyl siloxane	18.4	Polymethyl α -cyanoacrylate	28.8
		Polyacrylonitrile	28.8

Note: because of difficulties in their measurements, published figures for a given polymer can range up to 3% on either side of the average figure quoted. More comprehensive data are given in Reference 6.

Table 18.14 Solubility parameters and partial polarities (*P*) of some common solvents

	δ MPa $^{1/2}$	<i>P</i>		δ MPa $^{1/2}$	<i>P</i>
Neo-pentane	12.9	0	Tetrachlorethane	19.2	0.01
Isobutylene	13.7	0	Tetralin	19.4	—
<i>n</i> -hexane	14.9	0	Carbitol	19.6	—
Diethyl ether	15.1	0.03	Methyl chloride	19.8	—
<i>n</i> -octane	15.5	0	Methylene chloride	19.8	—
Methyl cyclohexane	15.9	0	Ethylene dichloride	20.0	0
Ethyl isobutyrate	16.1	—	Cyclohexanone	20.2	—
Di-isopropyl ketone	16.3	0.3	Cellosolve	20.2	—
Methyl amyl acetate	16.3	—	Dioxane	20.2	0.01
Turpentine	16.5	0	Carbon disulphide	20.4	0
Cyclohexane	16.7	0	Acetone	20.4	0.69
2,2-dichloropropane	16.7	—	<i>n</i> -octanol	21.0	0.04
Sec. amyl acetate	16.9	—	Butyronitrile	21.4	0.72
Dipentene	17.3	0	<i>n</i> -hexanol	21.8	0.06
Amyl acetate	17.3	0.07	Sec. butanol	22.0	0.11
Methyl <i>n</i> -butyl ketone	17.5	0.35	Pyridine	22.2	0.17
Pine oil	17.5	—	Nitroethane	22.6	0.71
Carbon tetrachloride	17.5	0	<i>n</i> -butanol	23.3	0.10
Methyl <i>n</i> -propyl ketone	17.7	0.4	Cyclohexanol	23.3	0.08
Piperidine	17.7	—	Isopropanol	23.4	—
Xylene	18.0	0	<i>n</i> -propanol	24.3	0.15
Dimethyl ether	18.0	—	Dimethyl formamide	24.7	0.77
Toluene	18.2	0	Hydrogen cyanide	24.7	—
Butyl cellosolve	18.2	—	Acetic acid	25.7	0.30
1,2-dichloropropane	18.4	—	Ethanol	25.9	0.27
Mesityl oxide	18.4	—	Cresol	27.1	—
Isophorone	18.6	—	Formic acid	27.5	—
Ethyl acetate	18.6	0.17	Methanol	29.6	0.39
Benzene	18.8	0	Phenol	29.6	0.06
Diacetone alcohol	18.8	—	Glycerol	33.7	0.47
Chloroform	19.0	0.02	Water	47.7	0.82
Trichloroethylene	19.0	0			

Note: a comprehensive list of solubility parameters is given in Reference 6.

Crystalline non-polar polymers and amorphous solvents Most polymers of regular structure will crystallise if cooled below a certain temperature, i.e. the melting point T_M . This is in accordance with the thermodynamic law that a process will only occur if there is a decrease in Gibbs free energy ($-\Delta F$) in going from one state to another. Such a decrease occurs on crystallisation as the molecules pack regularly.

Since a process only occurs when accompanied by a decrease in free energy there is no reason why a crystalline non-polar polymer should dissolve in a solvent at temperatures well below the melting point. However, as the melting point is approached the $T\Delta S$ term in the equation:

$$\Delta F = \Delta H - T\Delta S$$

increases (where T is the absolute temperature, ΔS the entropy change and ΔH the enthalpy change) so ΔF can become negative and solution may occur.

Hence at room temperature there are no solvents for polyethylene, polypropylene, poly-4-methyl-pentene-1, polyacetal or polytetrafluoroethylene, but at temperatures of about 30°C below their melting point solvents of

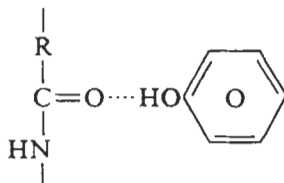
similar solubility parameter are effective. It should also be noted that at room temperature swelling may occur in the amorphous zones of the polymer in the presence of solvents of similar solubility parameter.

Amorphous non-polar polymers and crystalline solvents This situation is identical to the previous one and occurs, for example, when paraffin wax is mixed into rubber above its melting point. On cooling the paraffin wax tends to crystallise, some of it on the surface of the rubber. Such a bloom is one way of protecting a diene rubber from ozone attack.

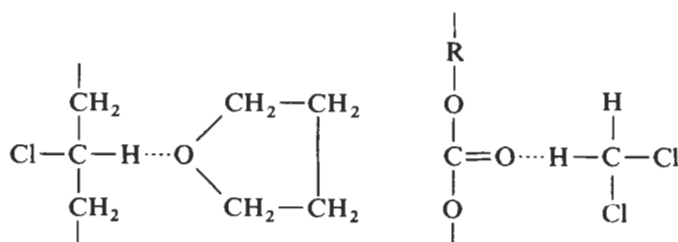
Amorphous polar polymers and solvents Molecules are held together by one or more of four types of forces, *viz.* dispersion, dipole, induction and hydrogen bonding. In the case of aliphatic hydrocarbons the so-called *dispersion* forces predominate. However, with many chemicals certain of the covalent bonds present are unevenly balanced, with one end being positively charged and the other negatively charged. Such *dipoles*, as they are called, can interact with dipoles on other molecules and lead to enhancement of the total inter-molecular attraction. Molecules which possess such dipoles and interact in this way by dipole forces are said to be *polar*. Many well-known solvents and polymers are polar, and it is generally considered that for interaction both the solubility parameter and their degrees of polarity should match. This is usually expressed in terms of partial polarity⁶ which expresses the fraction of total forces due to dipole bonds. Some figures for partial polarities of solvents are given in Table 18.14 but there is a serious lack of quantitative data on the partial polarities of polymers. At the present time a comparison of polarities has to be made by a common sense rather than a quantitative approach. For example, hydrocarbon polymers would be expected to have a negligible polarity and would then be more likely to dissolve in toluene rather than diethyl ketone, although both have similar solubility parameters.

Crystalline polar polymers and solvents It has already been pointed out that at temperatures well below their melting point crystalline non-polar polymers will not interact with solvents, and similar considerations can apply to a large number of polar crystalline polymers. It has, however, been possible to find solvents for some polar, crystalline polymers such as the nylons, polyvinyl chloride and the polycarbonates. This is because of specific interactions between polymer and solvent that may often occur, e.g. by hydrogen bonding.

For example, nylon 66 will dissolve in formic acid, glacial acetic acid, phenol and cresol—four solvents which not only have similar solubility parameters but also are capable of acting as proton donors whilst the carbonyl groups on the nylon act as proton acceptors:



A more interesting example is given with p.v.c. and the polycarbonate of bis-phenol A, both slightly crystalline polymers. It is noticed here that whilst methylene chloride is a good solvent and tetrahydrofuran a poor solvent for the polycarbonate, the reverse is true for p.v.c. yet all four materials have similar solubility parameters. It would seem that the explanation is that a form of hydrogen bonding occurs between the polycarbonate and methylene chloride and between p.v.c. and tetrahydrofuran. In other words there is a specific interaction between each solvent pair.



Many studies have been made to try to assess the propensity to hydrogen bonding of chemical structures. As a result the following broad generalisations may be made:

1. *Proton donors* include highly halogenated compounds such as chloroform and pentachlorethane. Less halogenated materials are weaker donors.
2. *Polar acceptors* include, in roughly descending order of strength, amines, ethers, ketones, aldehydes and esters, with aromatic materials usually being more powerful than aliphatic.
3. Some materials such as water, alcohols, carboxylic acids and primary and secondary amines may be able to act simultaneously as proton donors and acceptors. Cellulose and polyvinyl alcohol are two polymers which also function in this way.
4. A number of solvents such as the hydrocarbons, carbon disulphides and carbon tetrachlorides are quite incapable of forming hydrogen bonds.

Rubbers and thermosetting plastics The conventionally covalently cross-linked rubbers and plastics cannot dissolve without chemical change. They will, however, swell in solvents of similar solubility parameter, the degree of swelling decreasing with increase in cross-link density. The solution properties of the thermoelastomers which are two-phase materials are much more complex and dependent on whether or not the rubber phase and the resin domains are dissolved by the solvent.

Resistance to Cracking in Aggressive Environments

It has been found with many rigid plastics materials that under stresses well below the normal yield stress, cracking occurs in environments where when free of stress the polymer will be unaffected. The mechanism for this stress-cracking phenomenon is not well understood and indeed there may well be

many different mechanisms in different circumstances. There do, however, appear to be four main types:

1. 'Solvent' cracking of amorphous polymers.
2. 'Solvent' cracking of crystalline polymers.
3. Environmental stress cracking.
4. Thermal cracking.

Of the instances of so-called 'solvent' cracking of amorphous polymers known to the author, the liquid involved is not usually a true solvent of the polymer but instead has a solubility parameter on the borderline of the solubility range. Examples are polystyrene and white spirit, polycarbonate and methanol and ethyl acetate with polysulphone. The propensity to solvent stress cracking is however far from predictable and intending users of a polymer would have to check on this before use.

In the case of crystalline polymers it may be that solvents can cause cracking by activity in the amorphous zone. Examples of this are benzene and toluene with polyethylene. In polyethylene, however, the greater problem is that known as 'environmental stress cracking', which occurs with materials such as soap, alcohols, surfactants and silicone oils. Many of these are highly polar materials which cause no swelling but are simply absorbed either into or on to the polymer. This appears to weaken the surface and allows cracks to propagate from minute flaws.

Thermal cracking appears to be similar, but in this case air is the aggressive environment, becoming active at 70–80°C with some polyethylenes.

The whole of this important subject is reviewed in detail by Howard⁷.

Diffusion

The efficacy of polymers when used to protect metals from corrosive environments is influenced by their efficiency as barrier materials. When applied to metals by some techniques, such as fluidised bed coating, there is always the danger of 'macro-diffusion' through 'pinholes' which are gross imperfections in the surface and which do not have to be visible to be very much greater than the dimension of penetrating molecules.

Assuming, however, that the film is continuous then the concern is with the permeability of the polymer to the corrosive fluids. This involves both the dissolution of fluid into the polymer, which will be determined by the conditions discussed previously, and the rate of diffusion of the fluid through the polymer. This has been discussed elsewhere^{1,8} in detail, but may be summarised as follows:

1. The lowest diffusion rates occur with crystalline polymers below the T_g , since there is very little space through which diffusing molecules may pass.
2. Amorphous polymer below the T_g has a somewhat higher permeability, but diffusion is still difficult.
3. For amorphous polymers above the T_g , i.e. in the flexible and rubbery states there is more space available through which diffusing molecules may pass, and so these materials show comparatively high diffusion rates with diffusing fluids.

4. For crystalline polymers between T_g and T_m the diffusion rate is very dependent on the degree of crystallisation.

Review of Commercial Plastics^{1,9}

Amorphous Thermoplastics

Polyvinyl chloride (p.v.c.) P.V.C. is one of the two most important plastics in terms of tonnage and shows many properties typical of rigid amorphous thermoplastics. More individually, it softens at about 70°C, burns only with difficulty and is thermally unstable. To reduce this instability, stabilisers are invariably compounded into the polymer.

Being slightly crystalline, there are few good solvents, the best known of which are nitrobenzene, cyclohexanone and tetrahydrofuran. When mixed with certain non-volatile solvents such as some phthalates, adipates and phosphates, flexible materials are obtained and which are referred to as *plasticised p.v.c.*

In order to improve toughness many rubbers and other soft polymers may be used as additives to modify the compound. Some copolymers based on vinyl chloride are available of which the most important are the vinyl chloride-vinyl acetate materials used in gramophone records, flooring compositions and surface coatings.

Polystyrene (PS) The volume of expanded polystyrene produced probably exceeds the volume production of all other plastics (excluding the polyurethanes) put together. At least half the weight of polystyrene produced is in the form of high impact polystyrene (HIPS)—a complex blend containing styrene-butadiene rubber or polybutadiene.

Styrene-acrylonitrile has improved heat resistance, oil resistance and slightly better impact strength.

Acrylonitrile-styrene-butadiene polymers (ABS) These are complexes of blends and copolymers of excellent toughness. Some recent modifications show a degree of transparency.

Poly(methyl methacrylate) Used mainly where high light transmission and excellent weathering properties are of greatest importance. This polymer is the most well known of a very wide range of acrylic polymers which find uses as rubbers, fibres, plastics, adhesives and surface coatings. The sheet forms (Perspex, Plexiglas, Orogas) are often of high molecular weight and dissolve only with some difficulty.

Methacrylates are components of AMBS and MBS plastics which are similar to ABS; they have improved clarity.

Polyvinyl acetate and derivatives Polyvinyl acetate is used largely for coating applications, but the derivative polyvinyl alcohol, will, providing there are some residual acetate groups, dissolve in water. Reaction products of polyvinyl alcohol with aldehydes such as polyvinyl formal and polyvinyl butyral are highly specialised materials.

Cellulose plastics These old established materials have limited chemical resistance. Ethyl cellulose is, however, often used in conjunction with

mineral oil for hot melt strippable coatings for protecting metal parts against corrosion and marring during shipment and storage.

Crystalline Plastics

Polyethylene With p.v.c., polyethylene vies as the most important plastics material in terms of tonnage. It is attacked by only a few chemicals, it is not swollen by water or solvents, but it is susceptible to environmental stress-cracking in the presence of certain detergents, esters, alcohols and silicones. Commercial materials vary in the regularity of their structure, the more regular grades having a higher density, rigidity and a lower gas permeability.

Polypropylene It has similar chemical properties to polyethylene but is less susceptible to environmental stress cracking. It may also be used at somewhat higher temperatures.

Other polyolefins A variety of other crystalline polyolefins are available such as polybutene-1 (improved creep resistance over polyethylene), poly-4-methyl pentene-1 (excellent temperature deformation resistance) and ethylene-vinyl acetate (greater flexibility).

Polytetrafluorethylene (p.t.f.e.) This polymer does not absorb water, has no solvents and is almost completely inert to chemical attack; molten alkali metals and sodium in liquid ammonia are the rare exceptions. Furthermore it does not soften below 320°C, is electrically inert and has a very low coefficient of friction. It is more expensive than general purpose plastics, requires special fabrication techniques, is degraded by high energy radiation, and has a low creep resistance.

Other fluorine-containing plastics These materials, in general, attempt to compromise between the exceptional end-use properties of p.t.f.e. and the processability of ordinary thermoplastics. Examples include polychlorotrifluorethylene, tetrafluorethylene-hexafluorpropylene copolymers (FEP resins) and polyvinylidene fluoride. Polyvinyl fluoride is available in film form (Tedlar) with excellent weathering resistance.

Polyamides (nylons) The main types of nylon are oil and petrol resistant, but on the other hand susceptible to high water absorption and to hydrolysis. There are a few solvents such as phenol, cresol and formic acid. Special grades include a water-soluble nylon, amorphous copolymers and low molecular weight grades used in conjunction with epoxide resins. Transparent amorphous polyamides are also now available.

Polyformaldehydes (polyoxymethylenes, polyacetals) These are physically similar to general purpose nylons but with greater stiffness and lower water absorption. There are no solvents, but swelling occurs in liquids of similar solubility parameter. Poor resistance to u.v. light and limited thermal stability are two disadvantages of these materials.

Other polyethers The chlorine-containing polyether 'Penton' has excellent resistance to mineral acids, strong alkalis and most common solvents. It is not recommended for use with oxidising acids such as fuming nitric acid.

Poly-2,6-dimethyl phenylene oxide (PPO) and certain related materials are similar to the nylons but have superior heat resistance. These polymers are somewhat liable to stress-cracking problems.

Several polyethers are used as intermediates in the preparation of polyurethane foams whilst others such as polyethylene glycol are water soluble.

Linear polyesters Polyesters may be obtained in a wide variety of forms including rubbers, fibres, films, laminating resins, surface coatings and thermoplastic moulding powders. The last named are somewhat similar to the nylons but are more rigid. Chemical applications would appear to be limited because of their sensitivity to alkaline solutions and hot water.

Polycarbonates and polysulphones These are tough materials with heat resistance better than most thermoplastics. They are resistant to attack by acids and alcohols but the polycarbonates are sensitive to alkalis.

Thermosetting Resins

These materials often have better heat resistance than thermoplastics. Thermosetting resins are used in a variety of guises including surface coatings, but as plastics they are most frequently used in moulding compositions and in laminates. The tensile strength of unfilled rigid thermosetting resins is of the same order as for amorphous thermoplastics, i.e. about 55 MPa, but this figure may be greatly affected by the choice of fillers. For example, polyester-glass chopped-mat laminates often have tensile strengths in excess of 100 MPa whilst figures several-fold higher may be achieved by using carbon or boron fibres with epoxide resins.

Phenol-formaldehyde (phenolic) plastics The chemical resistance is affected by the phenol used, cresols giving the best acid resistance whilst xylenols are often used to obtain the best alkali resistance. For chemical-resistant applications the fillers used in moulding powder and reinforcing material in laminates should be inorganic, e.g. asbestos or glass. The resins are usually dark in colour.

Aminoplastics In this group, melamine-formaldehyde resins with their good heat resistance, scratch resistance and stain resistance, are usually preferred to urea-formaldehyde resins where chemical resistance is important. Unlike the phenolics these materials are not restricted to dark colours.

Polyesters It is possible to prepare polyester-based laminates without application of external heat and pressure thus facilitating the manufacture of large objects using simple equipment. The laminates have somewhat limited chemical resistance, being attacked by many acids, alkalis and organic solvents. Glass fibre is the common reinforcing agent and in some products there is a tendency for capillary action to occur up the bunches of fibre strands. Distilled water in general is more active in this respect than aqueous salt solutions including sea-water.

Epoxide and furan resins These materials, somewhat more expensive than the polyesters, may also be fabricated without the use of pressure, and at

ambient temperatures if so desired. They have markedly superior chemical resistance to the polyesters, particularly to alkalis.

Silicones This term is given to a wide range of polymers including fluids, rubbers and thermosetting resins. Although rather expensive relative to most other plastic they are particularly noted for their thermal stability and their water repellency.

Polyurethanes These are another class of polymers that are available in a wide range of forms, including rigid and flexible rubbers, surface coatings and adhesives. The solid polymers including the rubbers have particularly good abrasion resistance. The polyurethanes as a class are somewhat lacking in resistance to acids and alkalis, and the prolonged action of water and steam.

Polymers with Enhanced Heat Resistance

Very often a desirable feature of a plastics material is its low softening point which enables it to be melt processed at temperatures much lower than those normally used for metals and inorganic glasses. The more sophisticated uses to which plastics materials have been put have, however, led to the demand for newer polymers with improved heat resistance to supplement those materials already available such as p.t.f.e. and the polycarbonates.

The maximum service temperature for which a polymer may be used in a given application depends largely on two independent factors:

1. the thermal stability of the polymer, particularly in air;
2. the softening behaviour of the polymer.

Two other factors which also often need to be taken into account are:

1. the flammability of the polymer, or a compound from it;
2. the smoke evolution characteristics of the polymer or its compound.

Thermal stability is largely concerned with chemical reactivity which may involve oxygen, u.v. radiation or depolymerisation reactions. The presence of weak links and the possibility of chain reactions involving polymer chains may lead to polymers having lower thermal stability than predicted from studies of low molecular weight analogues.

The softening behaviour of a thermoplastic material depends to a large extent on the flexibility of the chain and the ability to crystallise. Significant cross-linking of a reasonably stiff-chained polymer will lead to material that is unlikely to soften below its decomposition temperature. Intermediate to the linear and cross-linked polymers are various 'ladder polymers' in which the polymer molecule consists of a pair of more-or-less parallel chains bridged in a manner analogous to the rungs of a ladder.

Resistance to burning depends on many factors. It is, however, to be noted that those polymers that only burn in air enriched with oxygen tend to have high carbon:hydrogen ratios and/or may also emit materials during degradation, such as hydrogen chloride, that are inherent flame-retardants.

Low smoke emission is also often associated with a high carbon:hydrogen ratio. Table 18.15 gives some collected data for the limiting oxygen index,

Table 18.15 Collected data for limiting oxygen index for a variety of polymers (unfilled)

<i>Polymer</i>	<i>Limiting oxygen index (%)</i>
Polyacetal	15
Poly(methyl methacrylate)	17
Polypropylene	17
Polyethylene	17
Poly(butylene terephthalate)	18
Polystyrene	18
Polyethylene terephthalate (unfilled)	21
Nylon 6	21-34
Nylon 66	21-30
Nylon 11	25-32
PPO	29-35
ABS	29-35
Polycarbonate of bisphenol A	26
Polysulphone	30
Polyethylene terephthalate (30% G. F)	31-33
Polyimide (Ciba-Geigy P13N)	32
Polyarylate (Solvay Arylef)	34
Polyether sulphone	34-38
Polyether ether ketone	35
Phenol-formaldehyde resin	35
Polyvinyl chloride	23-43
Polyvinylidene fluoride	44
Polyamide-imides (Torlon)	42-50
Polyphenylene sulphide	44-53
Polyvinylidene chloride	60
Polytetrafluoroethylene	90

Note: % of oxygen in air is 20.9

Polymers below line burn with increasing difficulty as the LOI increases.

the minimum percentage of oxygen in an oxygen/nitrogen mixture that will sustain combustion under a specified set of test conditions.

Polyimides obtained by reacting pyromellitic dianhydride with aromatic amines can have ladder-like structures, and commercial materials are available which may be used to temperatures in excess of 300°C. They are, however, somewhat difficult to process and modified polymers such as the polyamide-imides are slightly more processable, but with some loss of heat resistance. One disadvantage of polyimides is their limited resistance to hydrolysis, and they may crack in aqueous environments above 100°C.

The *polyether imides* show much better hydrolytic stability with little change in tensile strength after exposure to water at 100°C for 1 year. These materials also show exceptional resistance to mineral acids, and are unharmed by most hydrocarbons including gasoline (petrol) and oils.

Polyethersulphone is the term given to certain polysulphones of improved heat resistance introduced by ICI. (In fact all commercial polysulphones are polyethersulphones.) Commercial polymers now have values of T_g ranging from 190 to 285°C, but the cost generally increases sharply with T_g , and those at the higher end of the range may only be available to special order.

Polyether ether ketones (PEEK) have been developed using polyether-sulphone technology. These materials crystallise, unlike the polysulphones, and have higher maximum service temperatures. They also have better resistance to hydrolysis at elevated temperatures than the polyimides.

Polyether ketones were introduced in 1986. These materials have the highest operational temperatures of any thermoplastic material.

Polyarylates are highly aromatic linear polyesters with high values of T_g (up to 194°C has been quoted) and which are self-extinguishing.

Polyphenylene sulphides, when glass-fibre filled, have high temperature ratings, second only to polyether ether ketones amongst thermoplastics. These materials often have better resistance to environmental stress cracking than the polysulphones and have found use in automotive applications because of their resistance to corrosive engine exhaust gases, ethylene glycol and petrol (gasoline).

Thermoplastic Rubbers

These materials have characteristics of both rubbers and thermoplastics. At room temperature they behave like cross-linked rubbers, but at elevated temperatures the cross-links effectively disappear (they are said to be heat fugitive) and the material may be processed as a thermoplastic. Unlike truly cross-linked (vulcanised) rubbers, these materials may be capable of dissolution in solvents, although not necessarily at room temperature.

S-B-S Triblocks are block copolymers consisting of a block of butadiene units flanked by blocks of styrene. Below the T_g of polystyrene blocks from different chains congregate into domains which act both as cross-links and reinforcing fillers. The polymers will dissolve in hydrocarbon solvents. Hydrogenated S-B-S materials have better resistance to ageing.

Thermoplastic polyester rubbers are also block copolymers of polyethers and polyesters. The polyester groups are capable of crystallisation and the crystal structures act like cross-links. These materials have good hydrocarbon resistance. Similar thermoplastic polyamide rubbers are also now available.

Thermoplastic polyolefin rubbers are usually blends based on polypropylene and ethylene-propylene rubbers. They are not resistant to hydrocarbons.

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18.7 Rubber and Synthetic Elastomers

In 1839 Charles Goodyear discovered that raw rubber when mixed with finely divided sulphur and heated to 150°C, changed from a soft deformable substance into a tough resilient material. This reaction was called vulcanisation. Rubber linings have been in use for some 130 years for the protection of substances against chemical attack. In 1855, J. H. Johnson took out a patent for spinning components made from metal covered with rubber, thus combining the strength and durability of the metal with the non liability to oxidation of the rubber. In 1857, Thomas Hancock published his *Personal Narrative* which included details of the outstanding resistance of natural rubber to chemical compounds. In his summary, Hancock described sheets of a mixture of one part of natural rubber to two parts of pitch for the protection of ships' hulls. He listed moulded articles made from hard vulcanisates which were resistant to acids, alkalis and chemical solutions and also mentions vulcanised sheet rubber for use as linings in chemical vessels.

The excellent chemical resistance of ebonite was recognised at this time, and patents for the use of ebonite as a lining material were applied for in 1874 by Thomson and Watson in Great Britain. In 1885, Lacollonge in France was granted a patent for a lining composed of an underlay of ebonite with soft rubber on the exposed surface. Whilst ebonite linings had proved satisfactory in static applications, they had proved to be unsuitable for transportation work due to brittleness. In 1924, B. F. Goodrich introduced the Vulcalock bonding system, which used a cyclised rubber-based primer, thus enabling soft rubber to be bonded directly to a metal substrate.

Prior to 1940, the use of synthetic elastomers in linings was negligible, but the advent of the Second World War, and the consequent loss of natural rubber sources to the Allies, led to the use of synthetic rubber, namely a styrene-butadiene copolymer which, whilst not having all the properties of natural rubber, proved to have adequate anti-corrosive performance.

The standard polymers used for rubber linings consist of materials that are cross-linkable macromolecules which, on mixing with suitable reactants that form strong chemical bonds, change from a soft deformable substance into an elastic material. These polymers include natural rubber and its corresponding synthetic, *cis*-polyisoprene, styrene-butadiene rubber, polychloroprene, butyl rubber, halogenated butyl rubbers, acrylonitrile-

butadiene rubber, ethylene propylene terpolymer (e.p.d.m.) and chloro-sulphonated polyethylene (Hypalon).

With natural rubber and *cis*-polyisoprene the normal cross linking agent used is sulphur. When mixed with natural rubber and heated, the sulphur reacts with the alpha methylenic carbon atoms of adjacent molecules, predominantly by S_1 and S_2 cross links. If a low percentage of sulphur is added, normally about 2% by weight on the rubber, the end product is a soft elastic material.

Ebonites on the other hand contain from 28% to 40% sulphur. When ebonite compounds are vulcanised, the available cross-link sites are saturated and no residual unsaturation remains. In ebonites the sulphur reacts to give two different types of links. About 5% of the sulphur reacts to form cross-links in the normal manner, whilst the remainder forms addition links along the molecular chain. It is the addition links that confer the rigidity to ebonites as the bulky sulphur groups restrict the movement of the molecules when the material is stretched. The greater the percentage of addition links the more rigid, and thus more brittle, the ebonite. Similar reactions are used for cross-linking acrylonitrile butadiene and styrene-butadiene rubbers.

Standard butyl rubber, which is a copolymer of isobutylene with about 2% of isoprene vulcanises in the same manner as natural rubber but, as it only contains a small proportion of polyisoprene, the cross-link percentage is much reduced. It is therefore not possible to make ebonite from a butyl rubber. The same vulcanisation chemistry, with some modifications, applies to ethylene-propylene terpolymers and brominated butyl rubber.

Polychloroprene and Hypalon are usually cross-linked with metal oxides which combine with reactive side groups in the polymer chain.

In general, the reaction mechanism of elastomeric polymers with vulcanisation reagents is slow. Therefore, it is natural to add special accelerators to rubber compounds to speed the reaction. Accelerators are usually organic compounds such as amines, aldehyde-amines, thiazoles, thiurams or dithiocarbamates, either on their own or in various combinations.

Together with the polymer and vulcanisation reagents, rubber lining materials will contain inert fillers such as carbon black, barytes or silicates like china clay. Other ingredients such as plasticisers, tackifiers, stearic acid, zinc oxide and antioxidants are also added to confer the required processing and physical properties on the lining. All the compounding ingredients used must contribute to the maximum chemical resistance of the finished compound coupled with the minimum leach resistance requirements.

Except for standard ebonites and the speciality ambient vulcanising or 'chemical cure' linings, most compounds have the capability of vulcanising both in an autoclave at 150° C or more and in ambient pressure steam or hot water at 100° C. Ebonites are of two types, the autoclave version for factory applications and a highly accelerated version for vulcanising on site at 100° C. Site-lining ebonites with their high acceleration levels are limited with respect to operational temperatures. At temperatures above 70° C, they tend to post vulcanise leading to increased hardness and subsequent brittleness. Leaching of excess, unreacted accelerator can also cause problems, especially in electroplating operations, where contamination may occur with the deposited elemental metal.

Ambient Temperature Vulcanising Lining

A great difficulty, especially on undeveloped sites, is the requirement to raise steam for vulcanising purposes. This problem gives rise to time/cost difficulties, especially with respect to the lining of very large tanks.

In the past 'chemical cure' linings have been employed on a wide scale. These linings, usually based on natural rubber or acrylonitrile-butadiene rubber consist of a standard lining compound with a chemical activator such as dibenzylamine incorporated in the formulation. Prior to the application of the lining to the substrate, the individual sheets of rubber are dipped or brush coated with carbon disulphide or a solution of a xanthogen disulphide in a solvent. The carbon disulphide or xanthogen disulphide permeates the rubber and combines with the dibenzylamine to form an ultra-fast dithiocarbamate accelerator *in situ*, and thus the rubber rapidly vulcanises at ambient temperature.

Such chemical cure methods have been used for many years but, due to the inherent hazards of flammability and toxicity of the system, are not accepted in several countries. Also, if all the exposed working surfaces have not been properly treated, unvulcanised areas may occur which would rapidly deteriorate when the lining is put into service.

In more recent years, lining compounds have been developed that vulcanise at ambient temperatures. Most polymers can be used for such compounds, although most materials are based on natural rubber, acrylonitrile-butadiene rubber and polychloroprene. These compounds contain accelerators which usually give rise to a material which has a delay in the onset of vulcanisation with a subsequent rapid rise in cross-link formation to give full vulcanisation in 6 to 8 weeks. Such materials, unless to be used within a few days of manufacture, are refrigerated to arrest the self-vulcanisation.

The ambient temperature vulcanising of these linings gave rise to exceptional ageing properties both at elevated temperatures and on weathering. This ageing resistance is due to the maximisation of cross-link density at room temperature by avoiding high temperature vulcanisation, with consequent loss of a proportion of the available cross-links.

An alternative to self vulcanising linings is to use prevulcanised rubber sheet linings. The system in modern use is often a butyl rubber from 1.5 to 4.5 mm thick to which is laminated a 1.5 mm thick layer of a polychloroprene compound for adhesion to the substrate. Bonding is carried out with a polychloroprene-based adhesive vulcanised at ambient temperature by the addition of an isocyanate. The system is most often used for lining simple geometry substrates. As it is not possible to ensure that the chemically resistant butyl layer is totally free from pinholes, it is preferable to use such linings in situations where the polychloroprene underlayer will not be attacked by prolonged exposure to the contained environment.

Polyurethane Linings

Whilst some standard elastomers such as natural rubber can be compounded to withstand many abrasive conditions, and to have an acceptable life span,

they are usually limited on severe abrasive duties. In highly abrasive conditions, the use of selected polyurethanes can considerably extend the working life compared with that obtained with standard elastomer linings.

Abrasion-resistant duties may involve abrasion in an aqueous phase or abrasion by dry particulate materials. The selection of the polyurethane type is most important to obtain the best results. Polyester-based polyurethanes perform best in dry abrasion due to their low hysteresis properties and excellent resistance to cut initiation and propagation. However, polyester polyurethanes are susceptible to hydrolytic degradation, and therefore polyether polyurethanes are normally used for aqueous abrasion duties.

Polyester polyurethanes are usually based on a blend of a quasi-prepolymer (polyester/MDI) and a diol/polyester suitable for spray-up operation. An alternative is to use a solvent-containing system using blocked curatives to give an extended pot-life of 2 to 3 hours enabling them to be brush, roller or spray applied.

Polyether polyurethanes are often based on a quasi prepolymer/diol blend reacted with a carbodiimide modified M.D.I. suitable for automatic mix-dispensers.

Excepting polyurethanes which are designed solely for chemical resistance, most abrasion-resistant polyurethanes do not have the chemical resistant capabilities of the other elastomers. Chemical-resistant polyurethanes have elevated temperature limitations, but have proved to have an adequate resistance range especially when contamination by oils and certain solvents have to be handled.

Material Properties

Properties of lining materials are dependent on the formulation and, with polyurethanes, the chemical structure of the final reacted material. The following data on material properties is based on the performance of standard lining compounds. The information given should not be assumed to apply to all linings based on a given elastomer as technological variations may occur from one supplier to another. Thus two linings of equivalent physical properties do not necessarily have the same chemical resistance and working temperature limits.

A summary of the chemical and abrasion resistances, and approximate operational temperature ranges of elastomers is given in Table 18.16. Further details of specific chemical resistances are given in Table 18.17. The maximum temperature of use will always be dependent on the chemical conditions prevailing. Abrasion resistance can be affected by the chemical environment if the exposed surface properties are changed by adsorption or chemical attack. The rate of material loss by abrasion will also vary according to temperature as the resilience etc. is dependent on prevailing temperature conditions.

In general, soft lining compounds made from natural rubber, *cis*-polyisoprene and styrene butadiene rubbers have good chemical resistance to a wide range of inorganic acids, alkalis and their salts and have good abrasion resistance at temperatures up to 100°C. The linings will resist temperatures down to at least -40°C in dynamic working conditions such as empty tank

Table 18.6 Summary of elastomer properties

<i>Elastomer</i>	<i>Abbreviation</i>	<i>Chemical resistance</i>	<i>Abrasion resistance</i>	<i>Temperature range (°C)</i>
Natural rubber C/S-Polyisoprene Styrene butadiene	NR IR SBR	Good resistance except oxidative chemicals, organics, oils, hydrocarbon solvents	Good	−30 to 100
Polychloroprene	CR	Satisfactory resistance; organics fair; poor with oxidative chemicals and hydrocarbon solvents	Fair	0 to 100
Butyl Bromobutyl Chlorobutyl	IIR BIIR CIIR	Excellent resistance; oxidative chemicals fair; poor with oils, solvents etc.	Limited	−40 to 120
Acrylonitrile-Butadiene	NBR	Good except for some organics and oxidative chemicals; oils very good	Fair	−10 to 100
Ethylene-Propylene	EPDM	As for butyl	Limited	−40 to 120
Chlorosulphonated polyethylene (Hypalon)	CSM	Excellent, including oxidative chemicals	Good	−20 to 100
Polyurethane, ester based	PUK	Hydrolysis resistance poor; oils and many solvents	Excellent	−20 to 80
Polyurethane ester based	PUK	excellent; good except for alkalies, oxidative chemicals and organics	Excellent	−20 to 80

Notes:

1. The comments given in this table are dependent on the composition of the final compound and may vary according to the material source.
2. Ebonites based on NR, IR, SBR and NBR generally have enhanced chemical resistance. Minimum working temperature and abrasion resistance ratings do not apply

wagons. They are not suitable for oxidative chemicals and many organic chemicals.

When compounded to form ebonites they show improved chemical resistance especially to carboxylic acids and may be used for some oxidative chemicals depending on type and operating temperatures. Ebonites can be compounded to be suitable for working temperatures up to at least 100°C, but, due to brittleness, are not normally suitable for sub-zero temperatures.

Polychloroprene and acrylonitrile-butadiene rubber compounds have satisfactory chemical resistance but, except for phosphoric acid, are not suitable for mineral acids at higher concentrations. However, they have good resistance to oils, acrylonitrile-butadiene rubber being the better, and so are often used in oil-contaminated aqueous environments. Generally, abrasion resistance is only fair. Normal maximum working temperature is about 100°C. Acrylonitrile-butadiene rubber ebonites are sometimes used especially where solvent contamination occurs, but are normally very brittle and so should be used with care.

Table 18.17 Chemical resistance rating of elastomeric compounds

Chemical	NR IR SBR		NBR		CR	IIR CIIR BIIR EPDM	CSM	PUK Ester	PUK Ester
	Soft	Ebonite	Soft	Ebonite					
Acetic acid	L	S	L	S	X	L	S	L	L
Alcohols	S	S	S	S	L	S	S	S	S
Aliphatic hydrocarbons	X	L	L	S	X	X	S	S	S
Ammonium hydroxide	S	S	S	S	S	S	S	X	L
Aromatic hydrocarbons	X	X	X	X	X	X	X	L	L
Brine	S	S	S	S	S	S	S	L	S
Chlorinated brine	X	S	X	S	X	L	S	L	L
Chlorinated hydrocarbons	X	X	X	X	X	X	X	L	X
Chlorine	X	S	X	S	X	X	L	X	X
Chromic acid 50%	X	X	X	X	X	X	S	X	X
Copper salts	S	S	S	S	S	S	S	L	S
Detergents	X	S	L	S	L	S	S	L	S
Esters	X	X	X	X	X	X	X	S	L
Ethers	X	X	X	X	X	L	X	S	L
Fatty acids	X	L	L	L	L	L	L	S	L
Ferric chloride	L	S	L	S	S	S	S	L	S
Fluosilicic acid	S	S	S	S	S	S	S	L	S
Formaldehyde	X	S	L	S	L	L	S	L	L
Formic acid	L	S	L	S	X	L	S	L	L
Hydrobromic acid 50%	S	S	L	S	L	S	S	L	L
Hydrochloric acid	S	S	L	S	L	S	S	X	X
Hydrofluoric acid 50%	L	S	L	S	L	S	S	X	X
Ketones	L	S	X	X	L	L	S	S	S
Mineral oils	X	X	S	S	L	X	S	S	S
Nickel salts	S	S	S	S	S	S	S	S	S
Nitric acid 5%	X	L	X	L	X	L	S	X	X
Nitric acid 20%	X	X	X	X	X	X	S	X	X
Phenol	X	S	X	S	X	L	X	L	L
Phosphoric acid 50%	S	S	S	S	S	S	S	L	L
Phosphoric acid 85%	S	S	S	S	S	S	S	X	X
Potassium hydroxide	S	S	L	S	S	S	S	X	X
Potassium salts (most)	S	S	S	S	S	S	S	L	S
Sea-water	S	S	S	S	S	S	S	S	S
Sodium hypochlorite	X	S	X	S	X	L	S	X	X
Sodium salts (most)	S	S	S	S	S	S	S	S	S
Sulphurous acid	X	S	X	S	X	L	S	X	L
Sulphuric acid 20%	S	S	S	S	S	S	S	L	S
Sulphuric acid 50%	S	S	S	S	S	S	S	X	X
Sulphuric acid 65%	X	S	X	S	X	L	S	X	X
Sulphuric acid 85%	X	X	X	X	X	X	S	X	X
Tin salts (most)	S	S	S	S	S	S	S	S	S
Urea	S	S	S	S	S	S	S	S	S
Vegetable oils	X	L	S	S	L	L	L	S	S
Water (raw)	S	S	S	S	S	S	S	S	S
Water (demineralised)	S	S	S	S	S	S	S	S	S
Zinc salts (most)	S	S	S	S	S	S	S	S	S

Notes

1. Chemical resistance is a guide only and may vary depending on the composition of the compound.
2. Chemical resistance stated is based on a temperature of 20°C. Performance at a higher temperature will depend on the chemical environment.
3. Mixtures of chemicals can often give a different effect.

Butyl rubber, halogenated butyl rubber linings and ethylene propylene rubber linings have excellent chemical resistance at temperatures up to 120°C. There are cases where butyl rubber linings have been subjected to temperatures down to -65°C without deterioration. Linings based on these polymers do not exhibit good abrasion resistance, which can only be rated as fair.

Chlorosulphonated polyethylene rubber (Hypalon) has excellent chemical resistance even to oxidative acids at elevated temperatures. When specially compounded it can have excellent abrasion resistance in some operating conditions.

As previously stated, polyurethanes do not have the degree of chemical resistance enjoyed by the other elastomers. Specially designed chemical resistant polyurethanes are suitable for use in dilute non-oxidative acids and salts, but are not normally suitable for alkalis. They show good resistance to oils and solvents. Maximum temperature of use is usually about 80°C, but this temperature is very dependent on the chemical environment.

Lining Selection

The resistant properties of a lining compound depend on the choice of polymer and the compounding ingredients added to form the final material. Thus there is a diversity of choice between the base polymers and also in various compounds based on the same polymer. The ultimate choice is usually that which will be cost effective for the environment to be resisted.

The selection process involves the defining of the working environment, including details of all chemicals plus any trace chemicals, working temperatures and pressures, pipe flow rates, abrasive particles and any other conditions likely to affect the lining performance. BS 6374:Part 5:1985 gives full details on exchange of information for satisfactory lining selection.

The most suitable lining is then selected, usually by the lining contractor, who will take responsibility for the choice. Most lining companies have detailed knowledge of the resistance capabilities of their lining materials and are best able to make the final decision.

Where no relevant experience is available for a given duty the selection will be determined by laboratory and/or in-plant testing. Chemical resistance properties are usually determined by observing the change in volume and weight against time for the given environment. Tests should be carried out over a long period, preferably one year minimum but, with experience, it is often possible to extrapolate test results from shorter test periods of two to three months. Measurements should be taken at a maximum of seven day intervals and presented graphically for visual evaluation. The test material should reach a steady equilibrium with the test environment with little further change in weight and volume. It is not possible to give definite maxima for all working conditions, but it is usually considered that a maximum of 15% volume increase is desirable.

Laboratory testing for abrasion resistance will usually only indicate differences between competing materials, and so may not prove the suitability of a lining for a particular abrasive environment. In a chemical environment, absorption or chemical attack on the lining material will affect the rate of

wear. If the surface of the lining is heavily absorbed or attacked by the contained environment the physical properties change for the worse and the wear rate will increase. It is preferable, where possible, to install test panels or pipe sections in an existing working environment on site to gain an accurate assessment of wear rate and life expectancy.

Bonding Systems

For satisfactory operation, the rubber lining must be adequately bonded to the substrate it is protecting. BS 6374:part 5 gives definitive load to peel levels for various elastomers, but it is usually required that, on separation, the rubber should tear rather than part either at the primer/rubber interface or the primer/substrate interface.

Modern bonding systems usually consist of a primer coat, often with a secondary tie coat, plus a tacky solution to assist in the application of the rubber. The bonding systems currently in use are usually suitable both for autoclave vulcanisation and vulcanisation at 100°C with atmospheric pressure steam or hot water. Ambient vulcanisation bonding systems have to be chemically active at the lower temperatures and are therefore specialist in nature.

Design and Fabrication of Equipment for Lining

Equipment designed for lining must be sufficiently rigid and robust to avoid deformation which could tend to damage the lining during transportation, installation and subsequent operation. Allowance has to be made for access and for venting of fumes during the lining process. In enclosed steel vessels there must be at least one manhole which, after lining, complies with BS 470:1984, plus at least one additional 75 mm minimum diameter outlet to allow adequate circulation of air. All branches, outlets and other connections should normally be flanged so that the lining can be extended over the flange face to prevent the ingress of corrosive material between the lining and the substrate. Where pads are used, drilled and tapped holes for fixings must not penetrate through the main shell to the rubber covered surface.

The design of pipework has to be such as to allow access to welds and bends for weld and surface preparation. It is preferable to use seamless tubing conforming to BS 806:1986. Where this is impractical, tubing in accordance with BS 1387:1985 is acceptable provided that the butt-welded joint seam does not restrict the bore by more than 0.25 mm.

The maximum length of straight pipe is dependent on the nominal bore. Bores between 25 mm and 40 mm should not exceed 2500 mm in length, from 40 mm to 65 mm, 4000 mm in length, and 80 mm to 600 mm, 6000 mm in length. Some rubber lining companies will exceed these lengths, especially on larger bore pipes, but this is not always to be recommended. All fittings such as bends, tees and crosses are preferably to be made to standard dimensions rather than, as special 'one off' design items.

In fabrication all welds to be covered must be continuous, smooth and free from pinholes, cavities, undercuts and other imperfections. Corner

welds should be radiused to a radius not less than the thickness of the lining to be applied.

Concrete structures should be constructed in accordance with BS 5337 or BS 8110 as appropriate. The concrete must be properly cured under shuttering, or a curing membrane, for seven days followed by at least 28 days open curing prior to the commencement of lining. Surfaces have to be free from voids and projections and are often screeded to give a satisfactory finish.

BS 6374:Part 5:1985 gives full details of design and fabrication requirements and it is advisable to consult this document as well as the lining contractor prior to arriving at the final design.

The Lining Process: Sheet Rubber Linings

The production of a rubber lining includes the preparation of the rubber compound followed by processing to form the lining sheet, substrate preparation, lining application, vulcanisation and inspection. All these stages require thorough quality control, especially compound manufacture and sheet preparation, as chemical resistance depends on satisfactory dispersion of the individual ingredients and undetected flaws in the sheet will cause problems in service.

The lining sheet is prepared by calendering in thin plies up to 1 mm in thickness, followed by combining the individual layers on the calender to form a finished sheet, usually between 3 mm and 6 mm thick. Alternatively, lining sheet can be manufactured by the roller die process in which the sheet is extruded and then passed through rollers to give the finished thickness. Extrusion is also used for the preparation of unvulcanised rubber tubes suitable for lining pipes up to 200 mm in diameter.

Substrate Preparation

All metal surfaces such as mild steel should be grit blasted, normally to SA 2.5 as defined in Swedish Standard SIS 055900. If the surfaces are contaminated with oil, grease or a chemical from previously used items, the contamination is usually removed by sweating in steam prior to grit blasting. Concrete surfaces must be clean and dry and any laitence must be removed as it will affect the bond of the lining. Preferably the surface should be grit blasted.

All surface dust, residues and debris left after blasting must then be removed. Within four hours of completion of the grit blasting, primers must be applied to the prepared surface. Where very large tanks are concerned which take a long period of time to prepare, it is normal to grit blast an area, clean off and then prime, such that the operation is carried out in stages. When all surfaces have been grit blasted and primed, all surface dust is removed and a second coat of primer applied. After the primer has dried, secondary tie coats are often applied followed by a tack coat solution.

Lining Sheet Preparation and Application

The rubber sheet is tailored to suit the substrate geometry. The edges of adjacent sheets are normally overlap jointed to avoid steps which could trap air, the joint angle being about 30° face to face. After tailoring, the surface of the sheet to be bonded to the substrate is either swabbed with a solvent or a coat of tack solution is applied. All solvent is then allowed to evaporate prior to applying the sheet to the prepared substrate. The prepared sheet is then positioned on the substrate and rolled or ironed down taking care to avoid trapping air between the sheet and the substrate.

Extruded or made-up tubes for pipe lining are coated with a tack solution and then slid into the pipe and inflated with air so that they loosely adhere to the wall of the pipe. The rubber tube is firmly applied to the pipe wall either by hand, using long handled rollers, or by drawing a suitable diameter plug through the pipe, thus expelling any air between the rubber tube and the pipe wall, and firmly attaching the rubber to the pipe.

Vulcanisation

Vulcanisation being a chemical reaction, is time/temperature dependant. In factory operations, vulcanisation is usually carried out in an autoclave using steam under pressure at temperatures up to 160°C . If the lined unit is a vessel too large to fit in an autoclave and has an adequate pressure rating, all outlets can be sealed and it can itself be pressurised. If this technique is employed then care must be taken, as a failure of the steam supply with consequent condensation, can cause a vacuum and subsequent collapse of the vessel.

Large, non-pressure vessels, which are usually lined on site in their final location, are normally vulcanised at 100°C using steam at ambient pressure or boiling water. Using such techniques, vulcanisation times will be extended and it is often necessary to shield the outside of the unit to minimise heat loss. Self vulcanising or chemical cure linings usually take up to eight weeks to fully vulcanise, but this process may be accelerated by injecting steam or hot air into the unit.

Polyurethane Linings

Polyurethane linings may be produced by spray-applied, build-up thickness methods, centrifugal casting for straight pipes, mould cast linings and pre-reacted sheet linings. High-quality reactive materials are usually produced in automatic mix dispensers which preheat, meter, mix and deliver the material to the required delivery point. As with rubber linings, the substrate is prepared by grit blasting followed by the application of a primer coat.

The polyurethane lining systems in use today are normally of the 100% solids type without solvents. The individual components, prepolymer and isocyanate are preheated and pumped to the mix/dispenser for metering and mixing. After mixing, the material is pumped through an orifice where it is

atomised and is then sprayed on the substrate. The substrate temperature rises due to the initial temperature of the applied polyurethane combined with reaction exotherm as the mixture cures. Modern polyurethane systems enable spraying to be continuous and so the required lining thickness is rapidly achieved.

Straight steel pipes up to 600 mm in diameter and six or more metres in length are usually lined by centrifugal casting. In this technique, the prepared preheated pipe is fitted with end caps and placed into the heated casting oven. Freshly mixed liquid polyurethane is then injected into the pipe which is then spun round its longitudinal axis until the polyurethane has cured to form a solid lining.

Pipe fittings such as bends, tees and crosses, unless large enough to enable spray application of the lining, are usually lined by casting using internal mould formers. The pipe fitting is assembled with the internal mould and preheated, the polyurethane mixture injected and the whole is oven cured.

Pre-reacted polyurethane sheet linings, usually made by cast moulding or centrifugal casting and slitting, are used for protecting surfaces against abrasion. They are not normally used for corrosive environment conditions as it is difficult to make a good joint seal between adjacent sheets to ensure a leak-free lining. They are usually tailored to fit the substrate geometry and attached with bolts which are subsequently protected by a polyurethane cap.

Inspection and Testing

It is essential that the lining is thoroughly tested prior to being put into service, as any faults could lead to substrate attack. Rectification of a failed unit is often very expensive, and there is also the risk of escape of corrosive contents which could lead to damage to the surrounding area. In the lining process, inspection and testing are carried out at each stage of the operation. All substrates are inspected prior to, and after, grit blasting to ensure they are suitable for lining.

The rubber lining is inspected before and after vulcanisation. A visual examination for mechanical damage, cuts, lack of adhesion, blisters and poor jointing is carried out over the entire lining surface. Continuity testing for pinholes is also carried out using either a high-frequency instrument based on a Tesla coil generating a high frequency discharge or a direct-current high-voltage instrument. Test voltages vary between 5 000 V and 50 000 V depending on the thickness and resistance of the lining being tested. The probe of the instrument is passed over the surface of the lining producing a corona discharge. The discharge concentrates at the point of any fault which is thus located.

Unless test coupons are produced alongside the lining, the only method of testing the vulcanisation state is with a hand hardness meter. A Shore 'A' or IRHD meter is used for soft rubber linings and a Shore 'D' meter for ebonites. The usual specification is that the hardness has to conform to $\pm 5^\circ$ of the specified hardness. There is no quantitative non-destructive test for the strength of the bond between the lining and the substrate and so such tests are usually carried out in the laboratory on a sample prepared from the materials used.

Elastomeric linings play an important role in industry where their resistance to highly corrosive environments allow many processes to be carried out in an economic manner. Major areas of use include heavy chemicals, dyestuffs, pharmaceuticals, electroplating, fertilisers, steel, foodstuffs, ore extraction, hydrometallurgical extraction of elemental metals and the water treatment industry.

Rubber lining is a specialist operation and should only be entrusted to competent, established companies who are continually developing lining material systems to keep ahead of the requirements of the process industries. Full consultation should always be held, prior to the final design stage, to ensure that the most-cost effective material specification is employed.

J. S. PITMAN

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18.8 Corrosion of Metals by Plastics

One important advantage of plastics over many other materials is their great resistance to deterioration; however, in some applications this inertness of the bulk of the polymer may be deceptive, as practically all plastics contain quantities of non-polymerised residues or by-products which remain after processing. Many also depolymerise or degrade slowly releasing reactive fragments which migrate readily from the plastic to neighbouring items (either to items in contact or confined in an enclosed air space with the plastic); these ageing reactions may often be induced or accelerated, e.g. by increasing temperatures, ultra-violet irradiation, aerial oxidation and the presence of certain impurities, especially acids and alkalis. Contaminants derived from plastics have produced many problems including the spoilage of foods, the build-up of toxic atmospheres and the corrosion of metals. It is only in recent years that the extent of the last of these has been realised, and with the widening use of plastics and the increasing sophistication of modern equipment new problems are developing rapidly within this general context.

Corrosion by plastics may be conveniently sub-divided into two categories, firstly that resulting from contact of the metal with plastic (contact corrosion) and secondly that resulting from enclosure of the metal with a plastic in a confined air space but not in direct contact (vapour corrosion). A phenomenon related to the latter category is corrosion caused by the decomposition products of heated plastics during processing, during disposal by incineration, in electric circuitry (particularly associated with overloading or short circuits) or in fires. Plastics giving the most corrosive products on thermal degradation are those containing organic halogens, typically p.v.c., halogenated synthetic rubbers, fluoro-plastics, certain fire retardant polyesters and chlorinated rubber paints. The special problems posed by vapours from fires were discussed in a recent symposium in Stockholm¹. A summary² of the work of the Australian D.S.I.R. on corrosion by plastics, lists the degradation products which result from heating a variety of plastics and discusses the corrosive and toxic effects of the vapours. Certain plastics may also be degraded by microbiological action to corrosive products—such reactions are usually restricted to polymers derived from naturally occurring materials, typically cellulose and drying oil derivatives or to susceptible additives which may include plasticisers, fatty acids and organic fillers.

As well as their action on metals, plastics may also actively corrode other polymers—in the author's experience for example, plasticisers from p.v.c. have softened and degraded paint coatings, vapours from a two-stage-cured phenolic moulding produced cracking and degradation of an adjacent polycarbonate switch mechanism, cresols from a cold-curing low-exotherm epoxide softened an ABS casing, and several instances of crazing of polymethyl methacrylate have been attributed to the action of vapours from adjacent plastics. These effects are, however, outside the scope of this section and will not be considered further.

Vapour Corrosion

Vapour corrosion may be defined as 'the acceleration of atmospheric corrosion of metals by traces of volatile contaminants'; typically these are volatile organic acids (particularly formic and acetic acids), but corrosion by other volatiles from plastics including hydrogen chloride, oxides of nitrogen, sulphur dioxide, hydrogen sulphide, phenol, amines and ammonia, has also frequently been reported. The subject was surveyed by Rance and Cole³ in 1958, and more recently by Knotkova-Germakova and Vlckova⁴, and by Donovan and Stringer⁵. These three papers deal largely with the effects of vapours from plastics in an undegraded (freshly manufactured) condition; additionally Knotkova-Germakova and Vlckova⁴ refer to corrosion arising during manufacture. Kennett² has reported on the effects of vapours arising from thermal degradation of plastics, and Cotton and Jacob⁶ have referred to corrosion by vapours from polyvinylchloride (p.v.c.) at moderate temperatures (above 70°C) and from fluorinated polymers at higher temperatures (above 350°C). Corrosion can also be caused by acids produced by microbiological decomposition⁷ Clarke and Longhurst⁸ investigating the effects of humidity, showed that below 70% r.h. corrosion in air containing acetic acid vapour was very slow but accelerated rapidly as the relative humidity was increased above 80%.

Table 18.18 summarises the reported vapour corrosion effects of a variety of plastics; references to the source of the information is given at appropriate places.

The available range of plastics is very wide with a variety of compositions and related properties within any one type description. Even when physical properties and formulation are specified, minor variations in trace additives, release agents, moulding cycles, etc. may have a considerable influence on corrosivity. Table 18.18 can therefore be considered only as a guide and even in this sense much more experimentation is needed to provide the full picture. In the present state of technology precise information is only likely to result from tests carried out on the material of interest; various suitable test methods have been described in the literature^{4, 8, 12, 18, 21}.

There are, however, certain materials used as ingredients in the manufacture of plastics, which almost invariably give a corrosive product. Included in this category are wood⁸, which is frequently used as a filler or as part of a composite; drying oils, used in paints¹⁸, adhesives, jointing compounds and linoleum²²; and esters of volatile acids frequently retained in certain cold setting formulations, especially some paints¹⁸.

Table 18.18 Summary of vapour corrosion effects of plastics

<i>Material</i>	<i>Severity of corrosion*</i>	<i>Volatiles evolved and remarks</i>
<i>Thermoplastics</i>		
1. Polyvinyl chloride (p.v.c.) (and other chlorinated thermoplastics)	Non-corrosive at ambient temperature (but see column 3); moderately, very corrosive at 70°C	Hydrogen chloride (HCl). May become corrosive at ambient temperature if irradiated with u.v. radiation or in the presence of certain contaminants, e.g. zinc ions ⁹
2. Fluorinated thermoplastics (e.g. p.t.f.e.)	Non-corrosive at ambient and moderate temperatures; very corrosive above about 350°C ¹⁰	Decompose to release HF and F ₂
3. Nitrocellulose	Slightly-very corrosive ¹¹	Oxides of nitrogen may be evolved progressively with ageing
4. Nylons (a) Nylon 6	Corrosive ¹¹	Acetic acid; formulations frequently contain acetic acid additions as molecular weight regulators
(b) Nylon 66	Non-corrosive ⁵	
5. P.V.A. (polyvinyl acetates and alcohols)	Non-corrosive-very corrosive	Acetic acid released; corrosivity dependent on conditions and formulation (degree of hydrolysis and presence of stabilisers and inhibitors)
6. Cellulose acetate	Slightly corrosive ⁴	Acetic acid may be released
7. Polyacetals (a) Homopolymer	Slightly corrosive ^{4,5} at ambient temperature, more corrosive above 40°C	Acetic acid and formic acid evolved (acetic acid may be used as an end-stopper)
(b) Copolymer (formaldehyde and 10% ethylene oxide)	Usually non-corrosive at ambient temperatures, corrosive above 45°C ⁵	Formic acid evolved (if arduous moulding conditions have been used, the polymer may be corrosive at ambient temperatures)
8. Polyolefines, polyesters, polycarbonates, polystyrene, polysulphone, polysulphone, polyphenylene oxide and polymethylmethacrylate	Non-corrosive ^{5,11} at ambient temperatures	
<i>Thermosetting resins</i>		
1. Cross-linked polyester ^{3,5,12,13} (a) Cold cured polyesters	MEKP catalyst and cobalt naphthenate accelerator – very corrosive. Other peroxide catalyst systems slightly-moderately corrosive. Irradiation or non-oxidising } non-corrosive catalyst	Formic and acetic acids evolved. Corrosivity is determined largely by the catalyst used, but is also affected by the formulation, in particular diethylene glycol gives more corrosive resins than does propylene glycol
(b) Hot cured polyesters	Non-corrosive-moderately corrosive	

*Refers directly to Zn, Mg and steel; but see page 18:95

Table 18.18 (continued)

Material	Severity of corrosion	Volatiles evolved and remarks
2. Phenolformaldehyde ³⁻⁵		
(a) Two-stage resins (via novolaks)	Moderately-very corrosive	Evolve ammonia and formaldehyde } very corrosive if undercured or if they are compounded with wood, flour fillers
(b) Single-stage cure (via resols)	Non-corrosive (if fully cured and containing only inert fillers)	
3. Amino plastics ³⁻⁵	Non-corrosive-slightly corrosive	
4. Epoxides ⁴⁻⁶		
(a) Cold cured	Non-corrosive-slightly corrosive	Amines ⁶ may be evolved from amine catalysed resins, and cresol ¹¹ from certain cold-curing low-exotherm formulations
(b) Hot cured	Non-corrosive	
5. Polyurethanes	Non-corrosive ⁵ at ambient temperatures	
<i>Rubbers⁴, elastomers and adhesives</i>		
1. Natural rubber		
(a) Non-vulcanised ⁵	Slightly corrosive on prolonged exposure	Formic and acetic acid evolved
(b) Vulcanised ^{5,14}	Slightly-moderately corrosive	Hydrogen sulphide and sulphur dioxide evolved
2. (a) Synthetic rubbers ⁵⁻⁶	Non-corrosive at ambient condition — most are corrosive above 100°C	Many are chlorinated and evolve HCl on heating; Hypalon may also emit sulphur dioxide ⁴
(b) Polysulphide rubbers (cold curing) ⁵	Moderately corrosive-very corrosive	Formic acid; the catalysts used are peroxides
3. Silicone polymers ^{5,15-17}	Non-corrosive-very corrosive	Acetic and formic acids. Some single-pack silicone sealants cure by hydrolysis of acetox groups releasing acetic acid and are very corrosive; some two-pack formulations evolve formic acid and are corrosive, and others are reputed to be among the most inert polymers
4. Phenol and ureaformaldehyde glues ^{3,5}	Slightly corrosive-very corrosive	Formaldehyde, phenol, ammonia and HCl may be evolved. Various acids and salts that yield acids (e.g. formic acid and hydrochloric acid) are used in cold-set formulations. Volatiles evolved during cure may be absorbed by the materials being bonded

Table 18.18 (continued)

Material	Severity of corrosion	Volatiles evolved and remarks
<i>Paints and lacquers</i> ^{3, 5, 18-20}		
1. Oleo-resinous (drying oil) type		
(a) Air drying (inert pigments)	Moderately corrosive-very corrosive	Formic acid, other volatile acids and aldehydes
(b) Stoving (inert pigment)	Slightly corrosive-very corrosive	Formic acid
		corrosivity may be much reduced by certain neutralising pigments, e.g. zinc oxide, calcium plumbate
2. Air-drying synthetic-resin paints		
(a) Chlorinated rubber (hydrocarbon solvent)	Normally non-corrosive but may become corrosive after exposure to u.v. light or high temperature	HCl
(b) P.V.A. based	Non-corrosive-very corrosive	Acetic acid
(c) Cyclised rubber, nitro-cellulose, shellac, acrylics, two-pack epoxides and polyurethanes	Non-corrosive-slightly corrosive (if solvent fully removed-typically 2 weeks drying)	May have volatile ester solvents, or contain traces of volatile acids and these may be retained for some time and be corrosive
(d) Synthetic stoving paints (epoxides, formaldehyde condensation polymers)	Non-corrosive (if fully cured)	

Contact Corrosion

Although less widely reported than the effects of vapours, contact corrosion has been a serious problem in packaging and in electronics¹⁵⁻¹⁷. As miniaturisation and sophistication of electronic devices has increased, the hazard presented by corrosion is often the limiting factor inhibiting the attainment of expected levels of reliability.

Semiconducting devices, switches and miniaturised v.h.f. circuits are all particularly sensitive to the slightest reaction on critical surfaces, and in devices calling for the highest levels of reliability even the most inert of the phenolic, epoxide and silicone resins are not considered to be fully acceptable¹⁷; corrosion of electronic assemblies may often be enhanced by migration of ions to sensitive areas under applied potentials, and by local heating effects associated with current flows.

Little comprehensive work has been carried out on contact corrosion, but some results on a range of polymers have been reported by Czech workers⁴. In general, plastics that give rise to vapour corrosion (Table 18.18) will also cause contact corrosion. Some qualification is needed to this statement, however, as much depends on the type of contact and the other ingredients in the polymer, e.g. a paint may give good protection to the metal to which it is applied, but the vapour may cause corrosion of adjacent metal items within an enclosed space.

Access of air and water will also affect the corrosion rate. Metal inserts in corrosive plastics are most actively attacked at the plastic/metal/air interfaces; with certain metals, notably aluminium²³, titanium¹⁰ and stainless steel, crevice effects (oxygen shielding and entrapment of water) frequently accelerate attack. Acceleration of corrosion by 'bimetallic' couples between carbon-fibre-reinforced plastics and metals presents a problem²⁴ in the use of these composites.

The chloride ion is the most frequent cause of contact corrosion, since chlorine is present in the many chlorinated plastics, and is also frequently retained in residual amounts from reactive intermediates used in manufacture. Thus epoxides usually contain chloride derived from the epichlorohydrin used as the precursor of the epoxide. In addition to the contaminants referred to in Table 18.18, various metal and ammonium cations, inorganic anions and long-chain fatty acids (present as stabilisers, release agents or derived from plasticisers) may corrode metals on contact.

Susceptibility of Metals to Attack by Contaminants from Plastics

The relative susceptibility of metals to atmospheric corrosion varies widely with the type of contaminant, e.g. zinc and cadmium, two metals that are used for the protection of steel in exposed environments, are both rapidly attacked by organic acids²⁰; on the other hand, aluminium alloys resist attack by organic acids but may be rapidly corroded by chlorides, especially at crevices or areas of contact.

Copper alloys are particularly prone to attack by long-chain fatty acids which are often present in sealing compositions, temporary protectives²⁵ and as trace additives in many plastics; under acid conditions ester plasticisers may saponify in the presence of copper giving rapid corrosion of the copper and accelerating degradation of the polymer.

Copper and silver tarnish readily in sulphide atmospheres, and copper in contact with sulphur-vulcanised rubber will sometimes react with the sulphur, devulcanising it in the process. The growth of conducting sulphide whiskers on silver is noteworthy as these whiskers may give rise to short circuits across silver-plated contacts. Ammonia has little effect on most metals, but traces will tarnish many copper alloys and cause stress-corrosion cracking of certain stressed brasses.

Various authors^{5,8,18} have investigated the relative susceptibility of a variety of metals to attack by the lower fatty acids; the results show that magnesium, lead, steel, zinc and cadmium are all rapidly attacked (Donovan and Stringer⁵, for instance, showed that zinc corrodes at a rate of 5 μm per surface per week at 30°C and 100% r.h. in air that contains 0.5 parts per million of acetic acid); copper and nickel are attacked less rapidly, and aluminium, tin and silver are resistant to attack.

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18.9 Wood

Wood is one of the oldest constructional materials. Historically it was important in world exploration and trade, and the defence of that trade, in the provision of merchant ships and navies. It was also important in the early days of railway engineering and in building construction. Although in many applications wood has been replaced by other materials, this renewable resource now supports the growing industries of manufactured wood products. Prominent amongst these are the panel materials chipboard, flakeboard, strandboard, plywood and blockboard, hardboard and softboard, wood-cement products and the products of the very large pulp and paper industries.

Wood is particularly valuable for many conditions which are corrosive to common metals (e.g. acids and external exposure), and for contact with foodstuffs and beverages. It is not subject to corrosion in the electrochemical sense of the term applied to metals, but in saline conditions it can be attacked by the products of metal corrosion (alkali and iron salts) where poor technology or unsuitable wood species are used. Although wood is attacked by both extremely alkaline and acid conditions, particularly those which are oxidising, it can be employed over a wider pH range than most other materials.

Most wood species are subject to some form of biological attack, a hazard not encountered by most other constructional materials. Fungal decay and attack by termites and other insect borers and marine borers are the main problems. The heartwood of many timber species and the sapwood of most species can be impregnated with wood preservatives to prevent these problems.

Physical Properties of Wood

Timber is derived from a great number of botanical species, and has a wide range of properties. Variability also occurs within a single species and in order to achieve acceptable levels of uniformity, selection by grading is necessary. The timber trade differentiates between softwoods and hardwoods, and the latter are again separated into temperate and tropical types. Hardwoods are derived from broad-leaved and mainly deciduous trees, which are anatomically more complex and differ in chemical composition

from softwoods, which are derived from coniferous and mainly evergreen species.

Timber is anisotropic and most of its properties differ in the three growth directions—longitudinal, radial and tangential. This is mainly due to the general orientation of fibres in a longitudinal direction, resulting in an enhancement of most strength properties in that plane^{1,2,3}. Density^{1,2} which is interrelated with other properties, has a wide range of values in different species, varying from 40 kg/m³ for balsa to 1230 kg/m³ for *lignum vitae*.

Wood has very useful thermal properties. Dry wood has a low thermal conductivity and a high heat capacity, and is resistant to thermal decomposition at temperatures up to 250°C for short periods of time.

The most important and most troublesome property of wood is its hygroscopic nature. Changes of moisture content in timber are accompanied by dimensional changes⁴ which are also anisotropic, being usually very small in the longitudinal direction, but substantial in the other two planes, the tangential movement being about double the radial movement. It is therefore necessary to saw logs longitudinally to relieve drying out stresses which would otherwise result in splitting. Drying⁵ or 'seasoning' is also necessary to avoid fungal attack on non-durable species. Moisture absorption or loss occurs mainly through the end-grain, so end-grain sealing greatly reduces moisture movement.

Timber from the outside of the tree (the sapwood) usually differs markedly in properties from the inner part (the heartwood). Sapwood is always pale in colour, is susceptible to biological attack largely because of the presence of nutrients, and is usually permeable, therefore lending itself to impregnation treatment with preservatives. The heartwood of different timber species varies widely in appearance, natural durability and permeability. Heartwood can vary from being indistinguishable from sapwood to being well defined and dark in colour. The timber species which give long service life in hazardous conditions are highly impermeable and have high natural durability. Permeable species, which can be properly impregnated with preservatives can also give long service.

The availability of different timber species^{1,2,6} varies considerably with economic and political conditions, and the effects of past exploitation.

Resistance of Timber to Weathering and Biological Degradation

Timber has a very good resistance to exterior exposure, especially species of high density. The main factors which contribute to surface degradation are the ultraviolet component of strong sunshine which gradually degrades the lignin-rich bond between fibres, the varying stresses set up by the cycling conditions of wetting and drying which cause further disruption, and biological degradation. Surface degradation can largely be prevented by paints and other surface finishes, renewed at suitable intervals.

The main hazard to timber is biological attack. In milder climates this is mainly 'rot' due to fungal infections together with insect borers. In hot

climates termites may be of overriding importance, and in marine situations the destructive effect of marine borers is of greatest significance.

The sapwood of all timber species is susceptible to attack, so the use of a durable species usually requires the removal of the sapwood. However, since sapwood can usually be fully penetrated with preservative by an impregnation treatment, an overall durable product can be obtained from the timber of small trees of a durable species containing a high proportion of sapwood.

The heartwood of various timber species shows a wide range of resistance to biological attack. The natural durability of heartwood is assessed by ground contact tests and according to survival, classified into five categories^{1,2,7}: very durable (>25 years), durable (15–25 years); moderately durable (10–15 years); non-durable (5–10 years); and perishable, (<5 years).

Timber species also vary in the treatability of the heartwood^{1,2,8} with preservatives in an impregnation plant, and are classified into four categories according to the depth of penetration which can be achieved: permeable (complete penetration); moderately resistant (6–18 mm lateral penetration); resistant (3–6 mm lateral penetration); and extremely resistant (no appreciable lateral and very little end-grain penetration).

There are, however, timber species of low natural durability which are impermeable and therefore cannot be effectively preserved. Such timbers can only be successfully used in dry situations. Likewise where preservative-treated timber is to be used in a situation of the highest hazard, long service life is best achieved by using easily treated species impregnated with a suitable preservative. Timber species that are difficult to treat can be incised to improve preservative penetration.

For outdoor applications including ground contact the most effective wood preservatives are creosote^{9,10} and copper/chrome/arsenic (CCA)^{9,10} applied using a vacuum/pressure process. Creosote is used for railway sleepers, telephone and electricity transmission poles, agricultural buildings and fencing. CCA preservatives chemically react with the wood and cannot be leached out. The treated timber is mainly used in buildings and fencing and can be painted.

Most building timbers out of ground contact, are impregnated by a double vacuum process using a clear solvent-type preservative incorporating a fungicide, an insecticide and a water repellent. It is the preferred treatment for profiled joinery timber as there is no distortion, and painting is permitted, as the solvent is volatile. An alternative treatment for building timbers out of ground contact, widely used in Australia and New Zealand, is impregnation with disodium octaborate using a diffusion process applied to freshly sawn green timber.

In the maintenance of exterior timber, the surface application of creosote or a decorative solvent-type preservative at suitable intervals adds greatly to service life.

For the remedial treatment of fungal decay and insect attack on timber in buildings, clear solvent-type preservatives applied by spraying all available surfaces are generally used, supplemented with wood preservative pastes to obtain deep penetration. Water-based emulsions are also used for wood-worm control. There has been a general move towards the use of those

fungicides and insecticides which present a lower risk of environmental problems, especially in housing.

Another category of treatment sometimes required is that against fire damage¹². Surface coatings meet most requirements, but in some situations impregnation treatments of permeable timber species with fire retardant salts is specified. Impregnation solutions are usually based on ammonium phosphate and borax, and are commonly combined with a CCA preservation treatment. Salt-type treatments are only suitable for indoor use, but organo-phosphorus resins can also be used in exterior applications. With manufactured wood products, such as chipboard, fire-retardant salts can be incorporated in powder form. Unprotected timbers of large cross section survive structurally in fires better than unprotected metal, as an outer layer of charcoal protects the inner wood.

Impermeable timbers have a good resistance to polluted atmospheres where acid fumes rapidly attack steel. Wood has given excellent service in the buildings of chemical works and railway stations. Permeable wood species and sapwood can suffer defibration problems caused by the sulphur dioxide of industrial atmospheres. Tile battens are particularly vulnerable. The heartwood of Douglas fir, pitch pine, larch, Scots pine/European redwood and many tropical hardwoods give good service in these conditions.

Developments in glued laminated structures and panel products such as plywood and chipboard raises the question of the durability of adhesives¹³ as well as wood. Urea-formaldehyde adhesives are most commonly used for indoor components. For exterior use, resorcinol adhesives are used for assembly work, whilst phenolic, tannin and melamine/urea adhesives are used for manufactured wood products. Urea and casein adhesives can give good outdoor service if protected with well-maintained surface finishes. Assembly failures of adhesives caused by exudates from some timber species can be avoided by freshly sanding the surfaces before glue application.

Wood in Marine Conditions

Of all the natural situations in which timber is used, marine conditions are considered the most severe, and only a few of the commonly available timber species can be relied on to give a very long service life. This elite of timber species includes oak, teak, mahogany, and pitch pine for boat building and greenheart for harbour works. These are all highly impermeable and naturally durable woods. Centuries of tradition in the successful use of these timbers impairs any judgement on the extent of the problems which would arise if other timbers were used for marine work. Until the voyages of discovery oak was very much relied on.

Fungal decay in boats and marine structures is mostly associated with rain-water penetration and bad ventilation. Although it is generally thought the decay risk is less in saline conditions, this problem is largely controlled by the selection of timber species. Insect borer damage is uncommon in woods used for marine work, as again the selection of species and the avoidance of sapwood largely eliminates this risk. However, serious problems can occur in the form of marine borers^{11, 14} and chemical decay arising from attack on the wood by the products of metal corrosion¹⁵.

Shipworm (*Teredo* spp.), a mollusc which burrows into wood for protection, was a considerable problem in the days of wooden sailing ships, and can still be troublesome in wooden boats and harbour installations, especially in warmer climates. Gribble (*Limnoria* spp.), a small wood-boring crustacean, also causes serious damage and operates in cooler waters. Dense, naturally durable tropical hardwoods, and permeable timber species impregnated with creosote or CCA preservative, give the best service life against these pests. Sheathing with other materials is also effective.

Chemical decay of the wood around fastenings in boats and marine structures, commonly known as 'nail sickness' is caused by attack on the wood by the products of corrosion, i.e. alkali and iron compounds. Corrosion of fastenings operates on differences in oxygen availability¹⁵ as in crack or crevice corrosion. Any part of a fastening which has access to oxygen and electrolyte becomes cathodic, producing alkali from sea-water. In situations where this alkali cannot be lost by leaching or diffusion it chemically attacks the wood, gradually solubilising extractives, hemicelluloses and the lower molecular sizes of cellulose. Hardwoods, because of their much higher hemicellulose content are less resistant than softwoods, showing more shrinkage and distortion in damaged areas, but many hardwoods have the advantage of higher impermeability. Corrosion takes place on the embedded parts of fastenings where oxygen access is poor, i.e. the anodic areas. The soluble iron salts migrate into the wood and gradually hydrolyse producing rust deposits and mineral acid.¹⁶ The latter causes softening and embrittlement of the wood by hydrolysis, converting long-chain cellulose into smaller molecular sizes.

Corrosion of fastenings is normally prevented by the use of highly impermeable woods (traditional boat-building timbers) and totally enclosed fastenings to control oxygen and electrolyte access. High standards of workmanship are required for the same reason. Where parts of fastenings or fittings are exposed they should be protected with highly impermeable coatings. It has been demonstrated that further protection can be obtained by the use of fastenings coated with suitable plastics^{15,16} so that the metal-electrolyte contact is eliminated. The use of plastic-coated fastenings could widen the application of more permeable timbers for boat building and marine work. Pressure creosoting also makes a valuable contribution towards making permeable woods used for harbour works proof against sea-water and oxygen penetration, thus reducing corrosion risks.

Another problem associated with the marine situation, particularly in hot climates, is surface defibration or 'furring' of ship's decking¹⁷ and other timber surfaces. Disruption is due to the growth of salt crystals in the wood surface in the alternating cycles of wetting and drying, and is often assisted by ultraviolet radiation damage to the lignin-rich bond between fibres. Damage is superficial in the case of impermeable woods, but can be very destructive to permeable timbers. This problem is minimised by the use of impermeable timbers and the regular maintenance of protective surface coatings.

Corrosive Liquids: Wood in Chemical Service

Wood in chemical applications¹⁸ gives remarkably good service in the most severe conditions. Impermeable woods give the best results as any chemical degradation is confined to the surface, and the breakdown products are generally less harmful than metal corrosion products. Because of its permeability all sapwood must be removed. The low heat conductivity of wood is a property of considerable advantage for conserving heat and wood is commonly used for hotwells.

Wood has a good resistance to a wide range of chemicals. The acid resistance is superior to that of most common metals. Iron begins to corrode at pH 5, whereas attack on wood commences at pH 2, and even at lower values proceeds at a very low rate. Wood has excellent resistance to acetic acid which is particularly destructive to most common metals. In alkaline conditions wood has good resistance up to pH 11.

Softwoods (pitch pine, Douglas fir, larch, and if available Southern cypress and kauri), because of their chemical composition (low hemicellulose, high lignin, and high cellulose content) are intrinsically more chemically resistant than hardwoods, especially for alkaline conditions where they are also less likely to produce coloured extracts (cf. hardwoods with tannins). Softwoods are generally of straighter grain than hardwoods which is an advantage in vat construction as it confers maximum strength and minimises the risk of distortion and permeability which could be introduced by sloping grain. (The longitudinal to transverse permeability ratio averages 10:1 for various wood species.)

Hardwoods (oak, teak, iroko, idigbo and many other tropical hardwoods) give excellent service in acid conditions such as metal cleaning operations. Greater impermeability and higher densities can be found in hardwoods, and these properties largely offset their intrinsically lower chemical resistance and poorer straightness of grain.

Wood is still a favoured material for constructing equipment used for handling chemical effluent.

Although the use of wooden vats has declined with the advancement and wider use of plastics and corrosion-resistant metals, selected wood can still be the most economical material to use. Many old vats are still giving excellent service in industry. Vats give their longest service when used for one continuous operation, thus avoiding shrinkage and contamination troubles caused by changing usage. Vats should not be painted as any barrier on the outside will raise the moisture of the whole cross-section to a level promoting fungal decay in all but extremely durable timbers. Nitric acid, chlorine and sulphur dioxide are all destructive to wood, attacking the lignin component and causing surface defibration. To prevent or minimise chemical attack on wood surfaces, protective coatings of various waxes, bitumen, chlorinated rubber, polyvinyl chloride, phenolic and furfuryl resins can be applied.

In recent years the plyvat has gained popularity. It is constructed of cold-moulded marine plywood and protected internally with suitable resin coatings. A variety of phenolic resin impregnated laminated wood products which have good chemical resistance (particularly against acids) are made by soaking beech veneers in solutions of phenolic resins, assembling and heat curing in plywood or moulded form.

Mildly Corrosive Liquids

The chief advantage of wood for containers is that many common species are free from harmful contaminants. For this reason wood had widespread use in the food and beverage industries, but it has now suffered severe competition from corrosion-resistant metals, plastics and paper products. Oak had a very extensive use in tight cooperage in the brewing industry, and its use for barrels still survives in the maturing of whisky and brandy and in the wine industries. Wood is particularly useful where acetic acid is present as this acid is corrosive to most common metals.

Wood is commonly used for the packing in large water-cooling towers associated with electricity generating stations. Tight control of mild pH values is essential to avoid chemical damage to the wood surfaces by over-softening or overchlorination of the water¹⁹. Biological degradation of wood by soft-rot fungi was first discovered in the softwood packing of cooling towers, and effective preservation has been achieved by impregnation with CCA preservative which cannot be leached out under proper operating conditions. With water-cooling towers which have outer wooden casings, defibration or 'furring'¹⁷ of the outer surface sometimes occurs, caused by permeable wood allowing water evaporation, which leads to crystal growth of salts from the water causing surface disruption. Impermeable timbers avoid this problem.

Staining of Wood

Impaired appearance of wood due to staining²⁰ by contaminating substances can also be considered as a type of degradation, and its avoidance is important in furniture, panelling and high-class joinery.

The commonest staining trouble is 'iron stain'—the blue-black stain caused by the interaction of soluble iron corrosion products and the natural tannins in wood. Hardwoods are generally more susceptible than softwoods. Steel wool should not be used for smoothing wood surfaces. Iron stains, if not too severe, can be removed with oxalic acid. Heavy contamination with soluble iron corrosion products usually results in migration and conversion to rust deposits in the wood.

Tannin-containing woods can also suffer from dark-brown stains produced by alkali, usually from a concrete or a detergent source. Conversely, fair-faced concrete can be similarly stained by the run-off water from unprotected hardwood surfaces. Some woods, e.g. afzelia, ayan and idigbo, give yellow contaminating dyes with alkaline detergents and should not be used in washrooms and kitchens.

Tannin-containing woods also darken with ammonia, a process which is usefully employed in darkening oak furniture by 'fuming'. Ammonia stains can originate from animal glue, amino-type adhesives and concrete additive sources, particularly where damp conditions exist.

Pink stains occur naturally in some acidic woods, e.g. oak and Douglas fir, but similar anthocyanidin stains can be produced in the wood of sycamore, maple, walnut, agba and sapele by acid-catalysed adhesives. A variety of enzymatic stains can be produced at mildly elevated temperatures in the

steaming and kiln-seasoning operations of various woods. These are notably pink stains in ash, reddish stains in beech, and brown stains in hemlock. Undesirable brown streaks or bands following the grain, sometimes occur naturally in oak, teak and afrormosia, but exposure to light reduces the differences, in some cases to normal.

With most woods, new surfaces first of all darken when exposed to light, particularly with teak and afrormosia, where any masking of portions of the surfaces of furniture can give blemishes. After full colour development, strong sunshine bleaches most woods to a common brown colour.

Summary of Degradation Problems Associated with Wood

Superficial Degradation

Colour change Caused by exposure to light, the effect is greatest with hardwoods and is important in furniture, panelling and joinery; any masked areas become blemishes. Strong sunshine bleaches most woods to a common brown colour.

'Weathered surfaces' The main factors involved are:

- (a) Degradation of the lignin-rich bond between fibres by ultraviolet component of strong sunshine.
- (b) Surface checking caused by the stresses and movement in the wetting and drying cycles.
- (c) In marine and chemical applications, surface defibration caused by repeated crystal growth of salts in the wetting and drying cycles.
- (d) Biological degradation especially by soft rot fungi.

Weathering results in gradually receding wood surfaces.

Chemical stains These occur in tannin-rich woods, especially hardwoods.

- (a) 'Iron stains', i.e. blue-black stains caused by the interaction of tannin with soluble iron corrosion products. Soluble iron corrosion products may also be converted to rust stains.
- (b) Dark-brown stains with alkali; usually from a concrete or detergent source.
- (c) Ammonia stains, produced in damp conditions from adhesive and cement additive sources.

Chemical attack Damage is superficial in the case of impermeable timbers, but is deep with permeable wood species.

- (a) Damage by industrial atmospheres, e.g. defibration by sulphur dioxide.
- (b) Damage to cooling tower packing and casings due to, for example, oversoftening and overchlorination of water.
- (c) Damaging chemicals to wooden vats, e.g. delignifying (defibrating) agents, chlorine, nitric acid, sulphites and sulphur dioxide, some of which are usefully employed in pulping processes.

'Nail sickness' Nail sickness is chemical decay associated with corroded metals in marine situations. Chemical degradation of wood by the products of metal corrosion is brought about by bad workmanship or maintenance, or unsuitable (permeable) timber species, all of which permit electrolyte and oxygen access which promotes corrosion. Chemical decay of wood by alkali occurs in cathodic areas (metal exposed; oxygen present). Softening and embrittlement of wood occurs in anodic areas (metal embedded; oxygen absent) caused by mineral acid from hydrolysis of soluble iron corrosion products.

Biological Degradation

Wood-rotting fungi These fungi are active in situations where the threshold value of 20% moisture content in wood is exceeded.

- (a) Wet-rot fungi: attack on all sapwood and the heartwood of non-durable species.
- (b) Dry rot (*Serpula lacrymans*): very active in buildings in damp situations.
- (c) Soft-rot fungi: fungus not apparent; usually surface degradation in wet or moist conditions.

Wood boring insects

- (a) Termites: very destructive; warm and hot climates.
- (b) Common woodworm (*Anobium punctatum*).
- (c) House longhorn (*Hylotrupes bajulus*): very destructive; softwoods.
- (d) Death-watch beetle (*Xestobium rufovillosum*): oak; associated with decay.
- (e) Wood-boring weevils (*Pentarthrum* and *Euophryum*): damp situations; associated with decay.
- (f) Powder-post beetle (*Lyctus* spp.): sapwood of ring-porous hardwoods.

Marine borers

- (a) Shipworm (*Teredo* spp.): a mollusc; tropical waters.
- (b) Gribble (*Limnoria* spp.): a crustacean; cooler waters.

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18.10 The Corrosion of Metals by Wood

Wood can cause corrosion of metals by direct contact and, in confined spaces, also by the emission of corrosive vapour. With rare exceptions, all woods are acid, and the principal corroding agent in both types of attack is volatile acetic acid.

Acetylated polysaccharides form part of the structure of wood, the acetyl radical constituting some 2–5% by weight of the dry wood. Hydrolysis to free acetic acid occurs in the presence of moisture at a rate varying from one species to another; a wood of lower acetyl content can liberate acetic acid much faster under given conditions than another wood of higher content^{1,2}. Small quantities of formic, propionic and butyric acids are also formed³, but their effects can be neglected in comparison with those of acetic acid. There is a broad, but only a broad, correlation between the corrosivity of a wood and its acidity. The chemistry of acetyl linkage in wood and of its hydrolysis has been examined in some detail⁴.

Contact corrosion may be reduced by the presence of natural inhibitors, such as tannins, in the wood, and will be promoted by sulphates and chlorides in it*, especially if mineral preserving processes involving these ions have been applied.

Influence of Moisture

The influence of moisture is fundamental, as it is with other forms of corrosion. Long-term contact tests⁵ with ponderosa pine, some treated with zinc chloride, in atmospheres at 30, 65 and 95% r.h. showed that at 30 and 65% r.h. plain wire nails were not very severely corroded even in zinc chloride-impregnated wood. At 95% r.h. plain wire nails were severely corroded, though galvanised nails were attacked only by impregnated wood. Brass and aluminium were also attacked to some extent at 95% r.h. Some concurrent outdoor tests at Madison, Wisconsin, showed that the outdoor climate there was somewhat more severe than a 65% r.h. laboratory test.

* Woods contain from 0·2 to 4% of mineral ash. This consists largely of calcium, potassium and magnesium as carbonate, phosphate, silicate and sulphate. Aluminium, iron, sodium and chloride are also present. Sulphate contributes 1 to 10% by weight, usually 2 to 4%, and chloride 0·1 to 5%.

These are useful quantitative results, but they will cause little surprise, since the user of wood will expect metals in contact with damp wood to corrode.

A degree of corrosion acceptable on the nails and fastenings on the outside of a packing case is not, however, acceptable on metal components inside, which the box is supposed to be protecting. Vapour corrosion is also governed by relative humidity and can occur whenever the internal humidity exceeds a critical value, as may happen for a few hours in the cold of the night even in quite good storage conditions. The critical humidity for corrosive attack has been reported^{6,7} as 75%.

Less and More Corrosive Woods

Table 18.19 lists woods whose aggressiveness by vapour corrosion has been quoted in a survey⁸, together with typical pH values of the aqueous extracts of these woods reported in another investigation⁹.

Table 18.19 Relative corrosivity of woods by vapour corrosion

<i>Wood</i>	<i>Classification in Defence Guide-3A⁸</i>	<i>Typical pH values</i>
Oak	Most corrosive	3.35, 3.45, 3.85, 3.9
Sweet chestnut	Most corrosive	3.4, 3.45, 3.65
Steamed European beech	Moderately corrosive	3.85, 4.2
Birch	Moderately corrosive	4.85, 5.05, 5.35
Douglas fir	Moderately corrosive	3.45, 3.55, 4.15, 4.2
Gahoon	Moderately corrosive	4.2, 4.45, 5.05, 5.2
Teak	Moderately corrosive	4.65, 5.45
Western red cedar	Moderately corrosive	3.45
Parana pine	Least corrosive	5.2 to 8.8
Spruce	Least corrosive	4.0, 4.45
Elm	Least corrosive	6.45, 7.15
African mahogany	Least corrosive	5.1, 5.4, 5.55, 6.65
Walnut	Least corrosive	4.4, 4.55, 4.85, 5.2
Iroko	Least corrosive	5.4, 6.2, 7.25
Ramin	Least corrosive	5.25, 5.35
Obeche	Least corrosive	4.75, 6.75

While certain reservations must be kept in view (i.e. there is not necessarily a correlation between pH and corrosivity, and different samples of the same species of wood show a wide scatter of pH values, which might well be even wider if differences in duration of seasoning were taken into account), the results of vapour corrosion tests nevertheless indicate a general correlation between quoted pH values and the corrosiveness of wood vapours. It may reasonably be concluded that a strongly acid wood, pH less than 4.0, is potentially dangerous, and a less acid wood, pH more than 5.0, is likely to be relatively safe.

Heat treatments of wood are dangerous, for although existing acid vapours may be expelled, further vapours are formed by accelerated hydrolysis.

Volatile acid hardeners such as hydrochloric acid and formaldehyde (which oxidises to formic acid) present in glues in plywood contribute to vapour corrosion, as can varnishes and paints⁸.

Wood preservatives appear not to affect emission of corrosive vapours from wood, suggesting that the hydrolysis of acetyl polysaccharides is chemical, not biochemical. Some copper-base preservatives can give enough leachable copper ions to cause galvanic corrosion of other metals, notably aluminium and steel.

Metals Affected

The metals most susceptible to corrosion by wood are steel, zinc, cadmium, magnesium alloy and lead. The susceptibility of zinc and cadmium is no argument against the galvanising or cadmium plating of steel, since these coatings much reduce the rate of corrosion of steel by contact with wood or wood vapours, although they will not give the high degree of protection which they provide in open exposure to marine or tropical atmospheres.

Aluminium is relatively resistant¹⁰. So also are copper, brass, tin and stainless steel, but these metals should not be used as thin coatings on mild steel as they promote rusting at any points of breakdown.

Bimetallic corrosion between two different metals (see also Section 1.7) embedded in damp wood, e.g. in the hull of a boat, can occur in two ways¹¹. If the metals are joined by a metallic conductor, then the formation of the cell

metal A/damp wood/metal B

will result in accelerated corrosion of the metal which has the more negative potential in this electrolyte. Savory and Packman¹¹ point out that even if two metals are not connected by a metallic path, and project from wood into sea-water, then two opposing cells are set up, the first as described above and the second

metal A/sea-water/metal B.

These cells are unlikely to have the same potential so that a net potential will exist and one metal will corrode preferentially and the other will tend to be protected. However, although this situation may occur in practice it is difficult to see how the explanation given by Savory and Packman is tenable. In action, accelerated corrosion can occur on an individual metal, by the action of a concentration cell

metal A/damp wood/sea-water/metal A.

Iron salts from rusting steel, e.g. a nail, have a strongly deleterious effect on wood, causing 'charring' and complete loss of strength.

Practical Conclusions

Contact corrosion Nails and fastenings in many non-durable wooden articles exposed to damp will outlive the useful lives of the articles, and their corrosion is of no great importance. Corrosion is, however, important in tile

and batten nails in roofs, fences and other more permanent structures. Unprotected steel should never be used. Galvanised steel is much better, and brass, copper, the more corrosion-resistant alloys of aluminium, and stainless steel, are likely to give even longer service.

Vapour corrosion The best way to pack articles made of metals susceptible to vapour corrosion is in boxes made of metal or of those plastics which do not themselves emit corrosive vapours⁸. If wood cannot be avoided, then the less corrosive kinds should be chosen. Dryness, good ventilation and the inclusion of water-vapour barriers should be sought. Other obvious measures are the avoidance of susceptible metals and the use of protective treatments and paints.

Recent Developments

Differential Oxygen Cell Corrosion

In addition to the basic corrosion mechanism of attack by acetic acid, it is well established¹² that differential oxygen concentration cells are set up along metals embedded in wood. The gap between a nail and the wood into which it is embedded resembles the ideal crevice or deep, narrow pit. It is expected, therefore, that the cathodic reaction (oxygen reduction) should take place on the exposed head and that metal dissolution should occur on the shank in the wood.

Alkaline areas around corroding nail heads were demonstrated by Pinion¹³ using phenolphthalein indicator. Pinion also measured the corrosion current which flowed between a bare steel rod and a similar rod embedded in wood both placed in aerated sea-water. This is an extreme case of the differential oxygen concentration cell; a less severe example is that of galvanised steel nails used to fasten wooden planks to oak frames. In the case of oak planks the oxygen content of the environment around the nail is uniformly low (due to the impermeable nature of oak) and no significant corrosion is observed in moist conditions. Relatively rapid corrosion can occur in a mixed wood construction. Beech is more permeable than oak, thereby facilitating the creation of a differential oxygen cell. The cathodic process generates hydroxyl ions which diffuse into the beech and the anodic process introduces ferrous ions into the oak.

Wood Degradation

Two mechanisms of wood degradation have been identified which can be linked directly to metallic corrosion. Nail sickness is a term which has long been used to describe the process by which soft and spongy areas of wood form around corroding fasteners. Cathodically generated hydroxyl ions attack the hemicelluloses, lignin and even the cellulose components of wood¹³ if present at sufficiently high concentrations. Because hardwoods contain higher proportions of hemicelluloses than softwoods, hardwoods can be severely degraded by alkali, but because they tend to be less per-

meable than softwoods there is less tendency for oxygen concentration cells to be set up.

Degradation of wood is also observed adjacent to anodic corrosion sites. Some metal ions, notably Fe^{2+} , catalytically decompose the cellulose components of wood. This significantly reduces the wood's fastener-holding ability.

Moisture Content and Corrosion

As outlined previously the moisture content of wood largely determines whether or not corrosion can occur. The moisture content of wood is reported in terms of weight percent, although it can be related to the relative humidity of the environment with which it is in equilibrium. A value of *ca.* 15% moisture content is generally taken to be the lower limit for corrosion of any metals to occur in commonly used softwoods¹⁴.

At moisture contents of 20% or above (equivalent to 80%, r.h. at 15°C) wood is at risk from rot. This risk together with the enhanced risk of fastener corrosion in damp wood was highlighted in a recent survey¹⁵ of roofspaces fitted with varying qualities of between-joint thermal insulation.

Treated Wood

There are two main reasons for treating wood: to provide flame retarding properties and to guard against rot. Flame retardants are usually inorganic salts such as phosphates, sulphates and borates, the cation being metal or ammonium. Bare steel screws and nails are not recommended for use in such flame-proofed wood; for this service more corrosion-resistant materials such as brass, silicon bronze or stainless steel are used. Galvanised, sheradised, zinc- and cadmium-plated fasteners have inadequate corrosion resistance. Some fire retarding chemicals now contain corrosion inhibitors.

Preservative treatments used to protect wood against insect attack and fungus-related decay¹⁶ are of two general types. Organic based treatments such as creosote and pentachlorophenol are applied in solution in organic solvents. They contribute little to the ionic conductivity of the wood and it is generally accepted that their presence in wood does not exacerbate corrosion problems. Indeed, creosote apparently acts as a corrosion inhibitor for many metals^{14,17}. Inorganic preservatives are often based on copper salts or oxides, sometimes in combination with arsenic and chromium in the form of oxides or oxyanions. Due to the presence of uncombined by-product salts and leachable copper ions there is a serious corrosion problem for several metals especially steel, zinc and aluminium embedded in wet or recently treated wood^{18,19}. Untreated wood is also very corrosive in these circumstances, but fungal decay should preclude its use at moisture contents above *ca.* 20%.

Since much of the wood in common use today for joinery, including external window frames and roof trusses, is redwood, such as *Pinus sylvestris*, preservative treatment is very necessary. However, whilst it is known that little corrosion of fasteners can take place in dry wood (<15% moisture

content) and that serious corrosion can be expected in wet wood (both treated and untreated) there is no firm evidence concerning the corrosion of metal fasteners in wood of normal (15–22%) moisture content²⁰. Research is in progress but this is a difficult corrosion environment to study. The electrical resistivity of wood in this moisture-content range is high, preventing the application of linear polarisation methods.

The results of one research programme²¹ indicate that copper-chromium–arsenic treatments are not corrosive towards galvanised steel and stainless steel in the moisture content range 15–22%.

Corrosion Prevention in Wood

Wood is an intrinsically corrosive medium which becomes more corrosive in certain circumstances. In dry conditions, where the moisture content cannot exceed 15%, any metal can probably be used without any precautions being necessary.

At normal moisture levels (ca. 15–22%) there is a definite, though ill-defined, corrosion hazard in certain woods for commonly used metals such as steel, whether bare or protected by zinc in any form. The choice of material to be used for fasteners is difficult and depends on additional factors including possible wood treatments. In untreated, and solvent-borne preservative-treated redwoods, galvanised steel is commonly used. In flame-proofed wood more corrosion-resistant metals, such as brass or even stainless steels, are necessary. The choice of metals for use in wood treated with inorganic preservatives, particularly those based on copper salts, is even more difficult because the necessary information does not exist. Galvanised nails and nailplates are still used but some users are looking to materials such as stainless steel. The long-term behaviour of stainless steels is not known; there may be a crevice corrosion or pitting problem with some grades.

Wood at moisture contents in excess of 20% is liable to decay, and above ca. 22% it is quite corrosive in both the treated and untreated conditions. Wet wood can be found in leaky roofs, in ground contact and in many outdoor locations. Coated steel, stainless steel and, less satisfactorily, galvanised steel fasteners are used. This appears to be largely because of the high cost of more suitable materials.

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19.1 Corrosion Testing and Determination of Corrosion Rates*

Corrosion tests provide the basis for the practical control of corrosion and therefore deserve a more exhaustive discussion than limitations of space will permit. A detailed description of all the procedures and devices that have been employed in corrosion studies in many countries will not be attempted. Instead, attention will be directed principally to underlying principles and to comments on the significance and limitations of the results of the test methods that are considered. Further details may be obtained from the references and from the comprehensive works by Champion¹ and Ailor².

Tests may be classified conveniently under three headings.

1. Laboratory tests, in which conditions can be precisely defined and controlled.
2. Field tests (tests in real environments), in which replicate test samples of metals or alloys—referred to as test coupons or specimens—are exposed to the actual environmental conditions expected in service, e.g. the atmosphere, the ground, the sea, etc.
3. Service tests, in which the test specimens—which may often take the form of manufactured components—are exposed to the particular conditions in which they are to be used, e.g. in process streams of chemical plant.

Laboratory tests, although often necessarily conducted under conditions that are not met in service, nevertheless have a number of advantages over the other types of tests. Because conditions can be controlled at will it is possible to identify the separate effects of a number of factors on the corrosion behaviour. These factors include the type and condition of the metal surface, the environmental composition, temperature and pressure, movement of the specimen relative to the environment, time of exposure and so on. Laboratory tests, at least in principle, also enable comparisons to be made under identical conditions of the relative corrosion behaviour of

* Abbreviations used in the text for specifications are as follows: BS, British Standard; ASTM, American Society for Testing and Materials Standard; NACE, National Association of Corrosion Engineers Standard; ISO, International Standards Organisation Standard. Further details of English-language specifications relevant to corrosion testing are given in Appendix 19.1B.

different metals and alloys and different protective schemes, e.g. coatings, environmental treatments, etc.

In many cases attempts will be made to accelerate the test to produce results in a shorter period of time than might otherwise be possible in field or service tests. Such acceleration is usually achieved by intensifying one or more of the controlling factors. Tests might be conducted at a higher temperature, with more corrosive media, with activation of the corrosion process by electrochemical methods, etc., with the object of enhancing the aggressivity of the test conditions. While accelerated test procedures are often used, the results should always be treated with careful consideration. It is not unknown for a protective system to fail to meet the requirements of an accelerated test, although showing satisfactory performance in normal conditions of use. Nevertheless, a number of such tests, particularly for atmospheric corrosion where rates of corrosion in real conditions are often low, are accepted and correlations have been established with real conditions.

Field tests do not have the uncertainties attached to accelerated laboratory tests since there is no attempt to adjust the controlling environmental conditions. The chief problem is obtaining reproducible conditions from one test to another. This is particularly the case with tests in the atmosphere. While broad classes of terrestrial atmospheres have long been recognised, e.g. tropical, rural, urban, marine, etc., difficulties remain that are associated with variations within these classes. In the 1980s steps were taken within ISO to rationalise the situation by producing a standard on classification of atmospheres (ISO/DIS 9223:1989). Other standards are available that provide guidance on the mounting and disposition of specimens for field tests (ISO/DIS 8565:1987) and for the statistical treatment of results where large numbers of specimens are used (see Reference 2 and ASTM G16:1984).

Service tests will be used (1) where the operating conditions cannot be successfully reproduced in laboratory tests, (2) where the environment does not occur naturally, (3) where real components, as opposed to test specimens, need appraisal, and (4) to confirm laboratory and/or field tests.

Often, all three types of test will be used sequentially. An example might be in the development of a coating to protect suspension cables for use on a bridge in a coastal region. The test programme could involve salt spray testing of candidate treatments in the laboratory, followed by field trials of the most successful materials at a site similar in aggressivity to the location of the final product and eventual testing at the site with loadings and positioning matching those of the end use. It would be expected that the number of candidate materials would decrease through this sequence of tests.

Irrespective of the method of test or the purpose for which it is made there are certain practical features which require attention and which will be necessary to achieve good reproducibility (by one operator) and repeatability (by different operators).

Test Procedures

Preparation of Surface

When the test is to be made to predict the performance of a material in a particular service, the ideal procedure would be to have the surface of the test-pieces duplicate the surface of the material as it would be used. Here, however, a complication is presented by the fact that materials in service are commonly used in several forms with different conditions of surface. Where the number of materials to be compared is large, it will usually be impractical to test all the conditions of surface treatment of possible interest. The best practical procedure, then, is to choose some condition of surface more or less arbitrarily selected to allow the materials to perform near the upper limits of their ability. If all the materials to be tested are treated in this way, and preferably with uniform surface treatment, the results of the test will indicate the relative abilities of the different materials to resist the test environment when in a satisfactory condition of surface treatment. Then, if it should be considered prudent or desirable to do so, the most promising materials can be subjected to further tests in a variety of surface conditions so that any surface sensitivity can be detected.

These remarks apply as well to the treatment of the surfaces of specimens to be used in tests in corrosion research projects, except here selection of a particular method of surface preparation is required so as to achieve reproducibility of results from test to test and amongst different investigators. Methods of preparing specimens are described in ASTM G1:1988 and ISO 7539-1:1987.

The final step in surface preparation should ordinarily be a cleaning and degreasing treatment to remove any dirt, oil or grease that might interfere with the inception or distribution of corrosion. The simplest test of a satisfactory surface condition in this respect is for the specimens to be free from 'water break' when rinsed with water after cleaning. As a final treatment for specimens to be weighed prior to exposure, a dip in a mixture of water and acetone or of alcohol and ether will facilitate quick drying and avoid water-deposited films. Specimens to be stored prior to weighing should be placed in a desiccator which, in best practice, should be sealed without grease³.

In addition to the preparation of the principal surfaces of the specimen it is essential to machine or grind any cut or sheared edges, since these could become sites of preferential attack. As a general rule, edge effects should be kept to a minimum by using specimens in which the ratio of surface area to edge area is large. With flat specimens a disc is best from this point of view, but other shapes may be more convenient and acceptable in many practical instances. When mass loss is to be used as a measure of corrosion, precision will be improved by providing a large ratio of exposed area to mass, and thin flat specimens or fine wires have obvious advantages.

For accuracy of weighing, it is usually necessary to restrict the dimensions of specimens to what can be accommodated on the common analytical balances. It must be borne in mind that where attack occurs in the form of a very few pits or in crevices under supports, the extent of this localised

attack may be determined by the total area of the test-piece, as it establishes the area of passive metal acting as a cathode to the few anodic areas. Thus, larger specimens, or the much larger surfaces that will often be involved in field or service tests, may give rise to much more severe localised attack under nominally the same conditions of exposure.

In certain tests it is sometimes desirable to eliminate any effects of a mechanically achieved surface condition by chemical treatment or pickling of the surface prior to test. This may be done in a pickling solution; alternatively, the test itself may be interrupted after sufficient corrosion has occurred to remove the original surface, the specimen then being cleaned and reweighed and the test started over again. Wesley⁴ found it to be desirable to pickle off about 0.008 mm from the surface of specimens in acid to improve the reproducibility of the tests.

With materials like the stainless steels, which may be either active or passive in a test environment, it is common practice to produce a particular initial level of passivity or activity by some special chemical treatment prior to exposure. With stainless steels this objective may be subsidiary to eliminating surface contamination, such as iron from processing tools, by treatment in a nitric acid solution which might also be expected to achieve substantial passivity incidental to the cleaning action (ASTM A380: 1988).

In studies of the behaviour of materials that may be either active or passive in the test environment, there would seem to be a real advantage in starting with specimens in an activated state to see if they will become passive, and to ascertain how fast they are corroded if they remain active. If passivity should be achieved after such an activated start, the material can be considered to be more reliable in the test environment than would be the case if by chance it managed to retain an originally induced passivity for all, or most of, the test period. It may also be valuable to know how fast the metal will be corroded by the test medium if activity should persist.

A procedure for testing previously activated specimens applied in studies of titanium was described by Bayer and Kachik⁵. Renshaw and Ferree⁶ also employed prior activation in their studies of the passivation characteristics of stainless steels.

In many cases there will be a need to test metal-coated specimens, e.g. galvanised steel, tin-plated copper, nickel-plated zinc, etc. It will then be necessary to test specimens in the completely coated condition and also with the coating damaged so that the basis metal is exposed. The latter condition will provide the conditions for galvanic action between the coating and the basis metal. With sheet specimens this condition is most readily achieved by leaving cut edges exposed to the test environment.

There may also be a need to consider the performance of pre-corroded test specimens. Apart from the fact that these conditions frequently arise in service it is also important for two other reasons. First, the presence of corrosion products or other surface layers may affect the access of constituents of the environment to the underlying metal surface—where the corrosion process occurs—and, second, in the case of alloys some pre-corrosion may lead to compositional changes in the surface. These factors should be taken into account in the application of any test method.

Marking Specimens for Identification

The simplest way to identify a specimen is to mark it with letters or numbers applied by stamping with a stencil or number punch. There is, of course, always the danger that the identification marks will be obliterated by corrosion. To guard against this, the several specimens in a test should be identified further by a record of their positions relative to each other or to their supporting device. Before specimens are taken from test their identity should be established in this manner unless inspection has already shown that the identification marks have been preserved.

Other means of identification can be used on specimens exposed to atmospheric corrosion. For example, where stamped letters cannot be expected to persist, identification may be provided by holes drilled in particular positions, or by notching the edges of specimens in particular places both in accordance with a template. Where severe corrosion is encountered, the identification by drilled holes is more permanent than that achieved by notching edges.

Other means of identification sometimes used satisfactorily involve chemical etching of the surface (not to be generally recommended), or the formation of letters or numbers by means of a vibrating stylus. The former is advantageous in studies of stress-corrosion cracking in which stamped symbols could lead to regions of stress concentration.

Number of Replicate Specimens

Practical considerations usually limit the number of replicate specimens of each kind that can be exposed for each period of test. At least two are recommended for obvious reasons, and if a larger number can be accommodated in the programme more valuable results can be secured—especially when it is desired to establish the reality of small differences in performance. For statistical analysis, five replicates are desirable. Accounts of statistical planning and analysis are given by F. H. Haynie in Reference 2 and in ASTM G16:1984.

In providing replicates for tests to be subjected to statistical analysis, it is necessary in the original sampling of the materials to be tested to ensure that normal variations in those qualities of the metals that might affect the results are represented in each set of samples.

In order to secure information as to changes in corrosion rates with time, as in atmospheric exposure tests, it is necessary to expose sufficient specimens to allow sets to be taken from test after at least three time intervals.

For *preliminary* tests where the number of test specimens that can be accommodated is limited, yet numerous materials are of possible interest, it is in order to expose single specimens. This may be more advantageous than limiting the compositions that can be investigated by exposing half the number of materials in duplicate. Probably the greatest advantage in exposing two specimens of a material instead of only one is in detecting gross errors, as in weighing, etc. rather than in any considerable improvement in the precision of the observations that may be made as to the relative behaviours of the metals tested.

Test of Fusion Welds

In view of the widespread use of welded joints in equipment and structures exposed to corrosion, it is necessary to know whether such welded joints will demonstrate satisfactory resistance to attack. It is not necessary to include welded specimens of all materials in a preliminary study to discover which of them have satisfactory resistance to a particular environment. Weld tests can be postponed until the preliminary selection has been made, or, alternatively, those materials expected in advance to be most likely to be resistant can be exposed in the welded condition so as to expedite the final answer.

There are several reasons for testing welded specimens. The first is to discover whether the weld itself will resist corrosion satisfactorily. A second purpose is to discover whether the heat effects associated with welding operations have been in any way detrimental to the corrosion resistance of the parent metal near the weld—as in the case of the so-called ‘weld decay’ of stainless steels (see Section 9.5). Since weld deposits may themselves be subject to a weld thermal cycle, it is necessary to include cross welds in the design of welded specimens for such corrosion tests. Further, a weld will generally constitute a stress concentration and, unless post-weld heat treated, will contain residual contraction stress. Thus, testing may be necessary to generate appropriate corrosion fatigue or stress-corrosion cracking data. The latter may follow ASTM standard G58:1985, ‘Practice for the Preparation of Stress-Corrosion Test Specimens for Weldments’, for example.

A weld bead included in a test-piece is, to some extent, peculiar to itself and may not necessarily be representative of nominally similar welds to be made by other welders under other circumstances. To this extent, results of tests on welds must be subject to some qualification in interpretation, having in mind that what will be disclosed principally will be the overall ability of the composition of the weld metal to resist the corrosive environment. In some cases, entrapped flux, craters, fissures, folds, surface oxides etc. may introduce localised corrosion that may or may not occur with all welds of the type studied (see Section 9.5).

The heat effects of welding are to an even greater extent peculiar to the particular test specimens used. They will be influenced by the welding process, by the skill of the welder, by the thickness of the metal welded, by the type of joint made, and by the geometry and mass of the surrounding structure in so far as they affect heating and cooling rates and areas over which these effects apply. Consequently, what happens to a particular welded test-piece has questionable general significance, especially when the result shows no apparent damage to a material known to be susceptible to welding heat effects in corrosive environments. It should not be assumed that high heat input during welding will represent the worst case. For example, with ferritic steels which are sensitive to hydrogen embrittlement stemming from environmental action, low welding heat input can be most detrimental because of the formation of hardened structures in the weld area. Moreover, the possible effects of multipass welding with attendant repeated thermal cycles must be recognised in design of a suitable test-piece.

With some materials, there are specific heat treatments that are known to reproduce the worst effects of the heat of welding. It is recommended, therefore, that in tests made to qualify a material for a particular service environment, in addition to the exposure of welded test specimens in order to observe effects of welding heat, specimens should be included that have been given a controlled abusive or sensitising heat treatment. As an illustration, austenitic stainless steels may be held at 650–700° for 0.5–1 h, followed by testing for susceptibility to intercrystalline attack as in ISO 3651-1 or -2:1976.

If such sensitised specimens remain as free from accelerated corrosion as the welded specimens do, then it can be concluded that no detrimental effects of the heat of welding need be anticipated in the environment covered by the test. However, if the sensitised specimens are corroded while the welded specimens are not, there will remain the possibility that, under some conditions of welding, difficulties due to the effects of the welding heat may be encountered, and appropriate action or the substitution of more reliable compositions will be required. Having in mind the effect of time in damage of this sort, it will be necessary to make a careful examination of the corroded specimens to detect the first signs of attack before it can be concluded that none has occurred. In assessing the significance of attack observed on drastically sensitised specimens, it is necessary to keep in mind that no similar sensitisation may result from good welding practice. Likewise, it should not be concluded that attack in a specific test environment will occur to a similar extent, or at all, in some quite different environment.

The evaluation of heat treatments or the effectiveness of stabilisation by limiting carbon content of these stainless steels can be determined by subjecting specimens to the ASTM standardised acid copper sulphate test or boiling nitric acid test (ASTM A262:1986; *see also* Sections 9.5 and 1.3).

Duration of Exposure

The duration of a particular test is likely to be determined by practical factors such as the need for some information within a particular limit of time, or the nature of the operation or process with which the test is concerned. Tests are rarely run too long; however, this can happen, particularly in laboratory tests where the nature of the corrosive environment may be changed drastically by the exhaustion of some important constituent initially present in small concentration, or by the accumulation of reaction products that may either stifle or accelerate further attack. In either case, the corrosivity of the environment may be altered considerably. Gross errors may result from the assumption that the results apply to the original conditions of the test rather than to some uncertain and continually changing conditions that may exist during the course of too extended a test period.

Rates of corrosion rarely remain constant with time. More often than not, rates of attack tend to diminish as a result of the formation of adherent insoluble corrosion products or other protective films originating in the environment (Fig. 19.1). Therefore, extrapolation of results of tests that are too short is more likely to indicate a lower resistance to attack than will

actually be observed over a prolonged period of exposure. To this extent, such extrapolation may be considered as conservative. At the worst, it may lead to the use of a more resistant material or a heavier section than is actually needed, or to the exclusion from consideration of some materials that might be much better than the short-time test results would indicate.

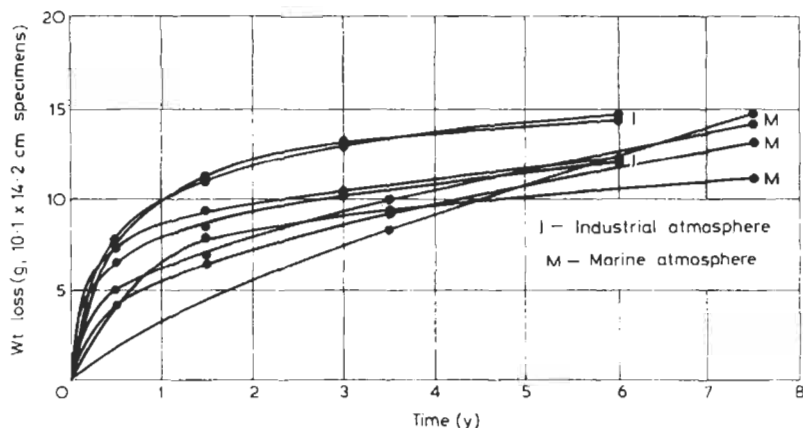


Fig. 19.1 Rate vs. time curve showing diminishing rate of attack (after *Proc. A.S.T.M.*, 51, 500, 1951)

Test should be of sufficiently long duration to permit demonstration of the possible protective nature of films, etc. Lengthy tests would not normally be required for materials that experience severe corrosion, although there are cases where this is not so. For example, lead exposed to sulphuric acid corrodes at an extremely high rate initially, while building up a protective film, then the rate decreases considerably and further corrosion is negligible. Short tests on such materials would indicate a high corrosion rate and be completely misleading. Short-term tests can also give misleading results on alloys such as stainless steels that form passive films. With borderline conditions, a prolonged test may be needed to permit breakdown of the passive film and subsequent more rapid attack. Consequently, tests run for long periods are considerably more realistic than those conducted for short periods.

Where anticipated corrosion rates are moderate or low, ASTM G31:1972 (R1985) suggests that the following equation be used to estimate a suitable test duration:

$$\text{Test duration (h)} = 50 / (\text{Corrosion rate in mm/y})$$

For example, where the corrosion rate is 0.25 mm/y, the test should run for at least 200 h.

Due to the relatively slow rate of the atmospheric corrosion process, it is recommended in ISO/DIS 8565:1987 that test exposures be on a schedule

such as 1, 2, 5, 10 and 20 years, depending on the corrosion resistance of the metal or coating being tested. In some cases, total exposure of less than 2 years may be suitable. It should be noted that, especially for short-term testing, the results may depend on the season of initiation of exposure. Therefore, it is recommended that exposures are commenced in the period of highest corrosivity (usually autumn).

Tests in waters and soils should ordinarily be allowed to run for extended periods in excess of 3 years, with removals of specimens in groups after different time intervals. A desirable schedule for any extended test in a natural environment is one in which the interval between successive removals is doubled each time. For example, the first removal would be after 1 year, the second after 3 years, and the third after 7 years, and so on. On the other hand, test periods should not be significantly longer than the process or exposure time of the end-use requirement. The testing of inhibitors for use if pickling or cleaning treatments should be of a period commensurate with the practical requirement which may be for only a few minutes.

In any event, the actual duration of a test must be reported along with the results, so that those who may wish to make predictions based on them will have an accurate idea of the extent to which they may undertake any extrapolation or interpolation.

Heat Treatment

Many alloys are subject to drastic changes in their response to the effects of corrosive media when they have undergone certain heat treatments. The principal effect of interest is a loss of corrosion resistance to some degree. This commonly takes the form of concentration of corrosion in particular regions or along certain paths — as in the vicinity of grain boundaries — where phases formed by heat treatment are most likely to be concentrated. In other instances, and particularly in castings, homogenising heat treatments may improve corrosion resistance by eliminating ‘coring’ or major differences in composition from point to point in the original dendritic cast structure. Heat treatments that eliminate internal stresses are obviously helpful in connection with stress corrosion, but may induce structural changes that can affect corrosion in other forms.

Heat treatments involving heating to a temperature high enough to take harmful phases into solution, followed by cooling (e.g. by quenching) at a rate fast enough to hold such phases in solution, may also be helpful in improving resistance to corrosion by avoiding attack that would otherwise be associated with a precipitated phase or compound.

Obviously, some knowledge of the possible effects of such heat treatments is essential for a complete understanding of the corrosion behaviour of an alloy. Studies along this line should follow upon the initial selection of a material considered to be possibly useful for a particular service. Thus, it should be tested in the condition most likely to resist corrosion. Sometimes the obtaining of this condition may require annealing at a temperature sufficiently high to take any possibly harmful phases or compounds into solution followed by quenching to prevent them precipitating. Following this preliminary selection, it would be prudent to carry out additional

corrosion tests on specimens that have been deliberately subjected to any possibly detrimental heat treatments to which the material may be subjected in processing, fabrication, or use.

Heat treatment may also affect the extent and distribution of internal stresses. These may be eliminated by appropriate annealing treatments which can remove susceptibility to stress-corrosion cracking. This must be explored in any studies of the performance of materials in environments where stress-corrosion cracking is a hazard. In particular cases, stress-relief annealing treatments may result in the appearance of new phases which, while eliminating the stress-corrosion effects, will induce another type of path of attack. This possibility must be kept in mind in assessing the overall benefits of heat treatments applied primarily for stress relief.

In other instances, heat treatments involving quenching, tempering, or holding at some temperature to precipitate an age-hardening compound are employed to secure some desired level of hardness or other mechanical properties. It is obviously necessary to explore what effects such heat treatments may have on the corrosion resistance of the material in the condition, or conditions, of heat treatment in which it is to be used.

Stress Effects

Techniques for studying effects of stress on corrosion are covered in some detail elsewhere in this work (see Section 8.10). So far as attention to stress effects in a general materials-selection programme is concerned, it is suggested that this should be a supplement to the initial selection of processing materials by exposing specimens in what approaches their best condition to resist corrosion, that is, free from stresses. Materials found to be worthy of further consideration in this way can be subjected to tests for stress effects. Where it is desired to discover whether severe internal stresses can be satisfactorily accepted, it will suffice to expose specimens in such a condition of stress. For example, a crucial test can be made by using a specimen in the form of a heavily cold-drawn tube in the as-drawn condition flattened on one end to introduce some additional multiaxial stresses. If such a severely cold-worked specimen suffers no stress-corrosion cracking in a test, then the danger of this occurring on any structure of that metal in the environment represented by the test is extremely remote.

Appraisal of Damage

There are many ways of determining the extent or progress of corrosion. The choice may be determined either by convenience or on the basis of some special interest in a particular result of corrosion or in a particular stage of a corrosion process.

Probably the most frequently made observation is the change in mass of a test-piece. This may take the form of a mass gain or a mass loss.

Mass-gain determinations are most common in studies of the extent and rate of oxidation or scaling at elevated temperatures (see ASTM G54:1984).

Very precise studies of this sort can be made by continuous observation of mass changes, as in the use of micro-balances, such as used and described by Gulbransen⁷. Such data have quantitative significance only when the exact composition (metal content) of the scale is known or can be determined and when there has been no loss of loose scale during or after the test. Fundamental studies of the initial stages of corrosion when films of a few monolayers are formed have made use of an ellipsometer to follow the increase of thickness of corrosion products without disturbing the specimen⁸.

In most other cases, data on gains in mass due to the accumulation of corrosion products have little quantitative significance since there is usually a question as to how much of the corroded metal is represented in the corrosion products that remain attached to the specimen at a particular time. There are also uncertainties as to the chemical composition of corrosion products, which may consist of mixtures of several compounds with varying amounts of combined or uncombined water, depending on the humidity of the atmosphere at the time.

For these reasons, it is much better to determine the amount of metal removed by corrosion by weighing what is left after removal of all adherent corrosion products by some method that will not cause further attack in the process, or by making a proper correction for losses in the cleaning process. (Removal of corrosion products is dealt with in detail in Appendix 19.1A.) Subtracting this final mass from the original mass will give the loss in mass during the test. Since the extent of this loss in mass will be influenced by the area exposed, as well as by the duration of exposure, it is desirable, in order to facilitate comparisons between different tests and different specimens, to report the loss in mass in a unit which includes both area and time. A most commonly used unit of this sort is milligrams weight loss per square decimetre of exposed surface per day (24 h) (mdd).

The unit $\text{gm}^{-2} \text{a}^{-1}$ (gma) is sometimes used in atmospheric corrosion tests (see ISO/DIS 9226:1989) where 'a' represents 'year'. It must be recognised that these units embody two assumptions that may not in fact be true. The first is that corrosion has occurred at a constant rate throughout the test period. This is rarely the case, since most rates of attack tend to diminish with time. But if the duration of the test and the actual loss in mass are also reported, the user of the data can take this into account. The second probable error in a mass loss/unit area unit is that it implies that corrosion has proceeded uniformly over the whole surface. These units, therefore, will give the wrong impression as to the probable depth of attack if corrosion has occurred at only a few spots on the surface of the specimen. Obviously, the mdd and gma units have limited significance when corrosion has taken the form of scattered pits or has been confined to the crevices where the specimen was supported. This should be covered by appended notes describing the nature and location of the corrosion represented and should be supplemented by data on the actual depths of the pitting or crevice attack. Here, again, the report should include data on the actual mass losses and duration of exposure.

Expression of mass loss in terms of a percentage of the original mass of a test-piece is usually meaningless except for comparing specimens of the same size and shape, since it does not take into account the important relationship between surface and mass.

As indicated, it is necessary to measure and report the depths of any pitting or other localised corrosion, such as in crevices, that may have occurred. It is also useful to provide information on the frequency of occurrence, distribution, and shape of pits, since these features are likely to have practical significance. Champion¹ has produced charts in which the number of pits/unit area, the size of pits, the depth of pitting, cracking and general attack can each be rated by the numbers 1 to 7. Where the number of pits is very large, it is obviously impracticable to measure the depths of all of them. Consequently, the practice has developed of choosing 10 of the deepest pits and reporting their average depth and that of the deepest of them. All surfaces of the specimen should be examined in selecting the 10 deepest pits.

There are several ways of measuring pit depths, but in all cases these measurements are facilitated if corrosion products are first removed (see Appendix 19.1A). If the pits are large enough, their depths may be measured directly with a pointed micrometer or with an indicating needle-point depth gauge. Otherwise, they may be measured optically with a microscope by focusing in turn on the surface of the specimen and, on the bottom of the pit using a calibrated wheel on the fine-focus adjustment rack for this focusing operation. In some instances the small dimensions or shapes of pits may require metallographic examination of a cross-section for a precise measurement of depth. Such metallographic examination may also be useful in detecting an association of pitting with a structural feature of the metal.

Since it is often difficult to visualise the extent of attack in terms of depth from such mass-loss units as mdd, it is common practice to convert these mdd figures into others to indicate depth of penetration, i.e. inches per year (ipy), mils or mm y⁻¹. Such calculations suffer from the same defects as the mdd figures in that they take into account neither changes in corrosion rates with time nor non-uniform distribution of corrosion. However, since such conversions are often made it is desirable for the initial reporter of the test results to make the calculations accurately and to report corrosion rates in both mdd and mm y⁻¹ or similar units.

The basic formula for making such calculation is:

$$\text{mdd} \times \frac{0.0365}{\rho} = \text{mm y}^{-1}$$

where ρ is the density of the metal in g cm⁻³. Some values showing the relationship between mdd, and ipy and mm y⁻¹ are given in Table 19.1.

Losses in mass will also not disclose the extent of deterioration that may result from the distribution of a very small amount of attack concentrated along grain boundaries or in transgranular paths (as in some cases of stress-corrosion cracking). In such instances, an apparently trivial or even undetectable loss in mass may be associated with practically complete loss of the strength or ductility of the corroded metal. Where this may be suspected, or in any doubtful cases, the mass-loss determinations must be supplemented by other means of detecting this sort of damage, including simple bend tests followed by visual or metallographic examination to disclose surface cracking, quantitative tension tests, and direct metallographic examination of cross-sections. Changes in electrical resistance have been used as a measure

Table 19.1 Relationship between corrosion rate in $\text{mg dm}^{-2} \text{d}^{-1}$ (mdd) and penetration in iny^{-1} (ipy) and mmy^{-1}

Material	Density (g cm^{-3})	Penetration equivalent to a corrosion rate of 1 mdd	
		$\text{ipy} \times 10^3$	$\text{mm y}^{-1} \times 10^2$
Aluminium 2S	2.72	0.528	1.342
Ambrac (Cu-6.5Si)	8.86	0.162	0.412
Brass (admiralty)	8.54	0.168	0.427
Brass (red)	8.75	0.164	0.416
Brass (yellow)	8.47	0.170	0.432
Bronze, phosphor (5% Sn)	8.86	0.162	0.412
Bronze (silicon)	8.54	0.168	0.427
Bronze, cast (85-5-5-5)	8.70	0.165	0.419
Cast iron	7.20	0.200	0.508
Copper	8.92	0.161	0.409
Cu-30Ni	8.95	0.161	0.409
Hastelloy A	8.80	0.163	0.414
Hastelloy B	9.24	0.155	0.394
Hastelloy C	8.94	0.161	0.409
Inconel 600	8.42	0.171	0.434
Iron-silicon alloy	7.0	0.205	0.521
Lead (chemical)	11.35	0.127	0.323
Monel	8.84	0.163	0.414
Nickel	8.89	0.162	0.412
Nickel silver (18% Ni)	8.75	0.164	0.417
Ni-resist	7.48	0.192	0.488
Silver	10.50	0.137	0.348
Stainless steel Type 304	7.92	0.181	0.462
Stainless steel Type 430	7.61	0.189	0.480
Steel (mild)	7.86	0.183	0.465
Tin	7.29	0.197	0.500
Zinc	7.15	0.201	0.510

of intergranular attack⁹. Because of the nature of such resistance determinations^{10,11} they have been more useful for comparing specimens of a particular kind and size than as a basis for quantitative expression of rates of attack.

The characteristic mode of corrosion of some alloys may be the formation as a corrosion product of a redeposited layer of one of the alloy constituents, as in the case of the brasses that dezincify, or of a residue of one of the components, as in the case of the graphitic corrosion of cast iron. Particularly in the case of the dezincified brass, the adherent copper is not likely to be removed with the other corrosion products, and therefore the mass-loss determination will not disclose the total amount of brass that has been corroded. This is especially important because the copper layer has very little strength and ductility and the extent of weakening of the alloy will not be indicated by the mass loss. In these cases, also, the mass-loss determinations must be supplemented by, or replaced by, mechanical tests or metallographic examination, or both, to reveal the true extent of damage by corrosion. Difficulties in obtaining accurate mass losses of heavily graphitised specimens have been reported¹².

Whenever changes in mechanical properties, such as performance in tension tests, fatigue tests, and impact tests, are to be used as a measure of

corrosion damage, it is obviously necessary to provide test data on the relevant properties of the uncorroded metal. When tests extend over long periods during which the alloys being tested may be subject to changes in mechanical properties due to ageing effects, entirely aside from corrosion, it will be necessary to provide sets of specimens that may be subjected to similar ageing in a non-corrosive environment so that by direct comparison with corroded specimens of the same age the changes due to corrosion can be separated from those due to ageing. Preferably the control specimens should be stored so that they will be subjected to the same thermal experience as the specimens undergoing corrosion. This is usually very difficult to accomplish while maintaining the control specimens completely protected from corrosion.

In calculating the strength properties of the corroded specimens and comparing them with those of the uncorroded control specimens after appropriate mechanical tests, it will be necessary to take into account the actual area of the cross-section of the corroded metal and report results on this basis instead of, or as well as, on the basis of the original cross-section prior to exposure such as would be represented by the uncorroded control specimens.

In view of possible or probable variations in mechanical properties among different specimens of the same metal cut from different sheets or other pieces, or even from different sections of the same sheet or piece, it is necessary to pay careful attention to the initial sampling of stock to be used for control, as well as exposure, specimens. An interesting case in which several of these considerations were involved was provided by the long-time atmospheric exposure tests of non-ferrous metals carried out by Subcommittee VI of ASTM Committee B-3 on Corrosion of Non-Ferrous Metals and Alloys¹³ in which changes in tensile properties were used as one of the means of measuring the extent of corrosion.

Tests carried out for particular purposes may make use of other special means to measure the progress of corrosion. For example, changes in the reflectivity of polished surfaces^{14,15} have been used as a sensitive means of following changes in the very early stages of corrosion in laboratory studies. A similar technique has been applied on a practical scale in connection with the direct evaluation of the relative merits of different alloys as used for mirrors in searchlights exposed to corrosive natural atmospheres.

Kruger¹⁶, while at the then U.S. National Bureau of Standards, used an ellipsometer to follow the growth of very thin corrosion-product films (oxides) during the initial stages of corrosion. This requires knowledge of the composition of the oxide and its refractive index. An outline of modern physical techniques for studying the nature and kinetics of the growth of oxide films and scales is given in Table 1.6, Section 1.2.

In some cases, the principal interest is in the possibility of undesired contamination or other alteration of an environment rather than in the rate of destruction of the metals being tested. Here, in addition to paying attention to the usual factors that influence rates of corrosion, it is necessary also to consider the ratio of the area of the test specimen to the volume or mass of test solution, and the time of contact. All of these factors may be quite different in a test from what would obtain in a practical case, and any dis-

tortions of the test in these ways must be taken into account in planning the test and in interpreting the results.

In cases such as this, the possible contamination of the solution by corrosion products may be estimated from the loss in mass of the test specimen. This, however, does not make any distinction between soluble and insoluble corrosion products, which may have different effects and which can be studied best by chemical analysis of the test solution and the materials filtered from it. Similarly, chemical analysis may be required to detect any other changes in the composition of the test solution that may be of interest.

Particularly in theoretical studies of corrosion processes, it has been useful to measure the progress of corrosion in terms of the rate or extent of consumption of oxygen in the corrosion reactions. This technique has been very useful in following the progress of wet corrosion or of oxidation in its initial stages¹⁷.

Somewhat along the same lines is the measurement of the volume of hydrogen generated as corrosion proceeds^{18,19}. This technique has been used not only in theoretical studies, but as a means of comparing some corrosion-resisting characteristics of different lots of steel which seem to affect their behaviour when used as a base metal for tin cans²⁰⁻²².

The polarograph has been found to be a very useful tool for following the progress of corrosion, especially in its early stages, by measuring minute changes in the composition of the solution, as in the consumption of some constituent, such as oxygen, or by the accumulation of metal salts or other reaction products, such as hydrogen peroxide²³.

An electrical resistance methods which directly measures loss of metal from a probe installed in the corrosive system under study is described in Section 19.3. It is reported that corrosion equivalent to a thickness loss of as little as 2.5×10^{-7} cm can be detected^{24,25}. This technique is most useful as a means of monitoring steps taken to reduce corrosion, e.g. by inhibitors, or to detect changes in the corrosivity of process streams. Electrical methods of determining corrosion rates are considered subsequently.

Temperature effects may also be used in test methods and notably for assessing the effects of inhibitors in acid solutions. The technique is based on that first proposed by Mylius²⁶ which records the temperature-time behaviour associated with the exothermic reaction resulting from the initial contact of a metal with a corrosive acid solution. The effectiveness of inhibitors may then be determined from their effects on the temperature-time behaviour²⁷.

Removal of Corrosion Products

An ideal method for removing corrosion products would be one that would remove them completely without causing any further corrosion or other deterioration of a test specimen in the process. Procedures that achieve this ideal or approach it very closely have been developed for many of the common alloys. Steels, for example, have been cleaned in such a manner that the loss due to cleaning is about 0.01%.

There are numerous satisfactory methods of cleaning corroded specimens, but whatever the method its effect in removing base metal should be determined for each material²⁸⁻³⁰ taking into account possible differences between the behaviour of 'as-new' and corroded base metal (see Appendix 19.1A). The various methods may be classified as follows:

1. Mechanical treatment.
 - (a) Scrubbing with bristle brush.
 - (b) Scraping.
 - (c) Wire brushing.
 - (d) Grit, shot sand blasting.
2. Chemical treatments.
 - (a) Organic solvents.
 - (b) Chemical reagents.
3. Electrolytic treatments as cathode in the following.
 - (a) Sulphuric acid usually inhibited.
 - (b) Citric acid.
 - (c) Potassium cyanide.
 - (d) Caustic soda.

Further details of removing corrosion products are given in Appendix 19.1A.

Laboratory Corrosion Tests

Total-immersion Tests

The total-immersion corrosion test is most adaptable to rigorous control of the important factors that influence results. This control may be achieved in different ways and it is unnecessary and undesirable to seek a standardised method or apparatus for universal use. All that is required is a recognition of what is essential, as covered, for example, by the ASTM procedure G31: 1972 (R1985). This represents a code of *minimum* requirements without insisting on the use of any particular kind of apparatus or specifying the exact conditions of aeration, temperature or velocity to be used. Since different metals respond differently to effects of aeration, temperature and velocity, the setting up of standard test conditions in terms of these factors would be inappropriate. Depending on the environment, such standardised testing conditions would favour maximum corrosion of some materials and minimum corrosion of others and thus lead to gross errors in indicating any general order of merit applicable under conditions differing from those of a standardised test.

In some instances it may be possible, though it is usually very difficult, to undertake laboratory corrosion tests under conditions that will be the same as those encountered in some practical application, and thus to secure some directly applicable data. More often, the conditions of service are so variable or so difficult to appraise accurately and duplicate in the laboratory that it is impractical and probably unwise to attempt to do so. A better procedure is to examine the individual effects of the several controlling factors by varying them one at a time so as to provide a picture of their influence on the

behaviour of the materials of interest in the corrosive medium being investigated. This information will be helpful in deciding whether the conditions of a particular use are favourable or unfavourable to the materials being considered. It will also serve as a guide to account for behaviour in service and to suggest changes in the operating conditions that may be expected to reduce corrosion of a material being used.

In many cases, and particularly in aqueous solution, the most important controlling factors will be solution composition, temperature, aeration and velocity.

Solution composition When designing tests to determine the effects of solution composition on corrosion it is important to understand the nature of the controlling process. In the case of most metals and alloys the rate-determining step will be the rate of supply of cathodic depolariser to the metal surface. This is particularly true in neutral solutions where corrosion will often be under oxygen diffusion control. Thus, tests in stagnant (unstirred, quiescent) conditions may be inappropriate since the effects of solution composition will be insignificant compared with the oxygen diffusion effect. In stagnant conditions corrosion rates of mild steel in, for example, sodium chloride, sodium sulphate and other salt solutions will be effectively the same over a range of concentrations and equal to that in pure water*. The effects of anion type and concentration begin to be shown only with movement of the solution, i.e. when oxygen access to the metal surface is facilitated to the point where it may be no longer rate controlling. Specific effects of anions in stagnant solutions will, however, be found when the anion has oxidising properties as in the case of nitrate.

Care must therefore be taken in designing tests to study the effects of solution composition since different results will be obtained depending on the degree of aeration and/or movement of the solution.

Variations in solution composition throughout a test should be monitored and, if appropriate, corrected. Variations may occur as a result of reactions of one or more of the constituents of the solution with the test specimen, the atmosphere or the test vessel. Thus, it is important that the composition of the testing solution is what it is supposed to be. Carefully made-up solutions of pure chemicals may not act in the same way as nominally similar solutions encountered in practice, which may, and usually do, contain other compounds or impurities that may have major effects on corrosion. This applies particularly to 'artificial' sea-water, which is usually less corrosive than natural sea-water. This subject is discussed in detail in a Special Technical Publication of ASTM³¹, and tests with natural, transported and artificial sea-water have been described³². Suspected impurities may be added to the pure solutions in appropriate concentrations or, better still, the testing solutions may be taken directly from plant processes whenever this is practical.

It should also be pointed out that in exploring the effects of the concentration of a particular acid or other chemical on its corrosivity, it is necessary to cover the full possible variation of concentrations thoroughly, since it

* An effect apparently first noticed by Heyn, E. and Bauer, O., *Mitt. K. Mater. Pruf Amt Berl-Dahlem.*, 28, 62 (1910)

frequently happens that particular ranges of concentration are especially corrosive to some metals. This extends to the highest degrees of concentration where sometimes the complete elimination of water may increase corrosion a great deal—as in the case of aluminium in acetic acid. On the other hand, the presence of a trace of water may make other chemicals much more corrosive—as in the case of bromine and other halogens.

It should be noted, also, that exposing a specimen to a solution of some chemical while it is being concentrated by evaporation practically to dryness will not suffice to explore the effects of the complete range of concentration, simply because the period in which any particular concentration range exists is not likely to be long enough to permit any especially corrosive effects to be detected in the overall result.

Temperature control Of the factors mentioned, temperature is probably the easiest to control; this can be accomplished by means of a thermostat or by operating at the boiling point of the testing solution with an appropriate reflux condenser to maintain the solution at a constant concentration. Control to $\pm 1^\circ\text{C}$ is not hard to accomplish.

The need for temperature cycling should be taken into account when designing or conducting tests. The nature of the test vessel should be considered for tests in aqueous solutions at temperatures above about 60°C since soluble constituents of the test vessel material can inhibit or accelerate the corrosion process. An inhibiting effect of soluble species from glass, notably silica, on the behaviour of steel in hot water has been shown³³. Pure quartz or polymeric materials are often more appropriate for test vessel construction.

Aeration Control of aeration is more difficult. Aeration here means the amount of oxygen supplied either as such or, more commonly, in air. In some situations, it may not require a large amount of air bubbled through a solution to accommodate even a modest rate of corrosion of a small test-piece. Figure 19.2 shows the relationship between the rate of supply of air used for aeration and the rate of corrosion of Monel alloy in 5% sulphuric acid.

To facilitate rapid solution of oxygen from air bubbles it is desirable to make these as small as possible, e.g. by having the air enter through a porous thimble or sintered glass disc. Much less satisfactory results are secured by simply letting air escape into the solution from a tube drawn to a fine tip.

It is also undesirable to permit air bubbles to impinge directly on the test-pieces. This can be avoided by placing the aerator inside a chimney.

When it is desired to study effects of various degrees of aeration, it is better to do this by varying the oxygen content of the saturating gas (e.g. by using controlled mixtures of oxygen and nitrogen) introduced at a constant and adequate rate than by attempting to vary the rate of admission of a gas (such as air) of constant composition. This extends as well to zero aeration, which can best be accomplished by saturating the test solution with de-oxygenated nitrogen or other inert gas. It is unwise to assume that, because no air is purposely added, oxygen has been excluded from a test solution in a vessel open to the air. Such a practice provides a low oxygen availability that is not sufficiently under control to ensure reproducible results³.

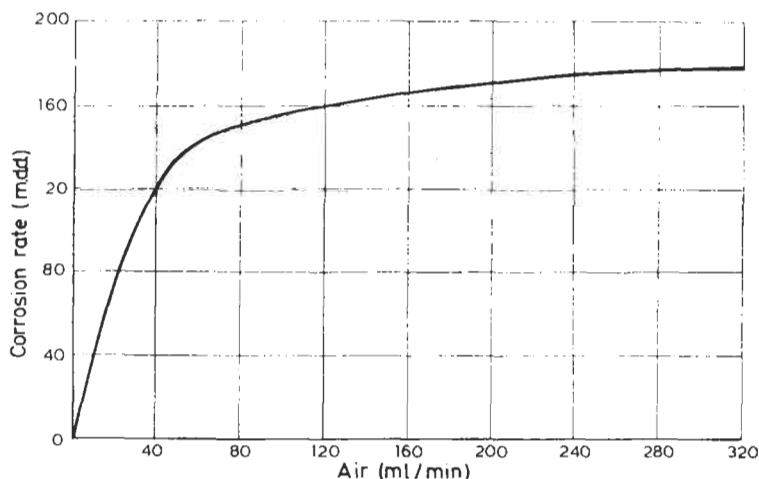


Fig. 19.2 Effect of rate of supply of air used for aeration on corrosion of Monel alloy in 5% sulphuric acid

Velocity The precise control of velocity and the study of effects of velocity on corrosion are extremely difficult, especially when high velocities are involved. A major problem is to prevent, or to take into account properly, the tendency of a liquid to follow the motion of a specimen moved through it, e.g. by rotation at high velocity. This can be controlled to some extent by proper baffling, but uncertainties as to the true velocity remain—as they do also when the test liquid is made to pass at some calculated velocity over a stationary test-piece or through a test-piece in the form of a tube or pipe³⁴.

Velocity effects can be achieved either by having the test-piece move through a presumably stationary liquid or by having a moving liquid come into contact with a stationary test-piece. Occasionally tests may involve both types of exposure. Details of test procedures are given in NACE TM 0270-70 *Method of Conducting Controlled Velocity Laboratory Corrosion Tests*.

The achievement of zero velocity in a test set-up is about as difficult as the accurate control of some high velocity. It is a common mistake to assume that by not making any attempt to move either the specimen or the testing liquid, the relative velocity between them will be zero. This neglects such effects as convection currents and the agitation due to the effects of corrosion products streaming under the influence of gravity. The most common difficulty arising from this situation is that these uncontrolled effects in tests made under presumably quiet or stagnant conditions make it very difficult to secure reproducible results from test to test. Therefore, even when there is no practical interest in the effects of any appreciable velocity, it is desirable to provide for some controlled movement of either the specimens or the solution at some velocity such as 7.5 cm s^{-1} , readily achieved with a vertical circular-path machine.

Equipment of this type in which the specimens are moved in a vertical circular path with all portions of the surface of a specimen moving at the same speed has been used where such moderate test velocities are required.

Statistical analysis of data from tests with an apparatus by Wesley⁴ has demonstrated satisfactory reproducibility of results not only among specimens in a particular test, but also from test to test undertaken at different times.

Where effects of much higher velocities are to be studied, various devices have been used to move test-pieces through the testing solution at high velocity.

One procedure is to use test specimens in the form of discs which can be rotated at the desired speed while either wholly or partly immersed in the testing solution, and Freeman and Tracy described a device of this sort in a contribution to the *ASTM Symposium on Corrosion Testing Procedures*²⁸. With their apparatus the specimen discs were mounted on horizontal shafts and were partially immersed in the testing solution.

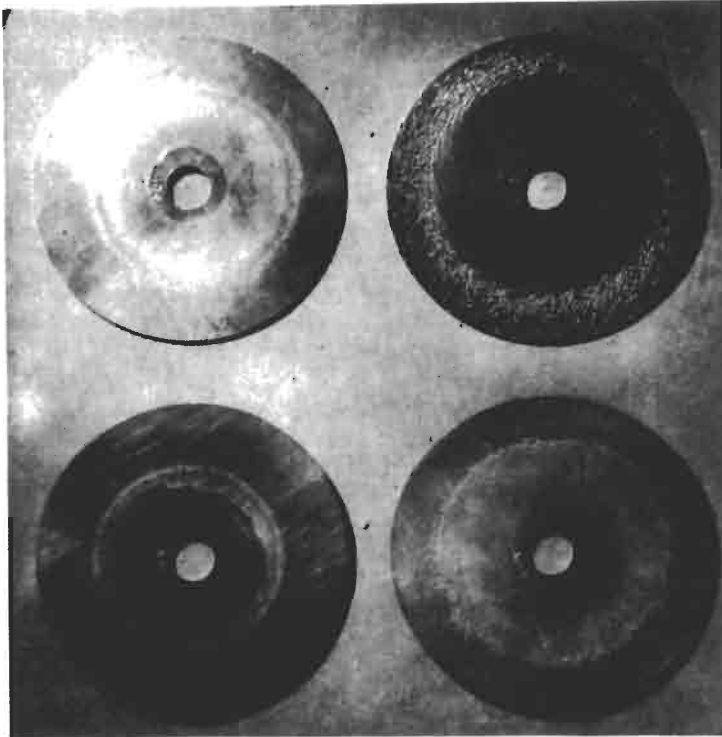
A similar method of test was used at the International Nickel Company's Corrosion Laboratory at North Carolina. The specimen discs are mounted on insulated vertical spindles and submerged in sea-water, which is supplied continuously to the tank in which the specimens are immersed. The maximum peripheral speed of the spinning disc is about 760 cm s^{-1} , and the characteristic pattern of attack is shown in Fig. 19.3a. Studies of variation of depth of attack with velocity indicate that at low velocities (up to about 450 cm s^{-1}) alloys such as Admiralty brass, Cu-10Ni and cupro-nickel alloys containing iron maintain their protective film with a consequent small and similar depth of attack for the different alloys. At higher velocities the rate increases due to breakdown of the film.

Tests of this sort indicate a sort of critical velocity for each material that marks the boundary between the maintenance and loss of protective films. These apparently 'critical' velocities must be considered as relative and only applicable to the conditions of test in which they are measured. Because of the complex effects associated with the differences in velocity from point to point on such rotating specimens, the apparent 'critical velocity' obtained in a given test may be quite different from what might be indicated by another test in which the same velocity is achieved in some other way — as by moving the liquid past a stationary specimen at a uniform velocity from point to point. The apparent 'critical velocity' indicated by this latter method of test will likely be higher for many materials than that shown by the spinning disc test. Thus, the establishment of critical velocities by a particular method of test will afford only qualitative data regarding the relative abilities of a number of materials to resist the destructive effects of high velocity. Furthermore, the critical velocity at which severe attack commences has been found to depend on the diameter of the disc so that no quantitative significance can be attached to it. This restriction extends as well to tests with iron discs, where attack is concentrated at the centre of the disc rather than at the periphery, irrespective of its diameter.*

Somewhat similar tests may be made by attaching specimens to discs that can be rotated at some desired velocity in the testing medium. A machine of this sort that is used extensively in studying corrosion of metals by sea-

* Small variations in solution composition may also affect the value of any critical velocity. In laboratory tests using recirculating artificial sea-water the presence of dissolved copper from copper alloy test-pieces has been shown to affect the value of the critical velocity for such materials³⁵.

(a)



(b)

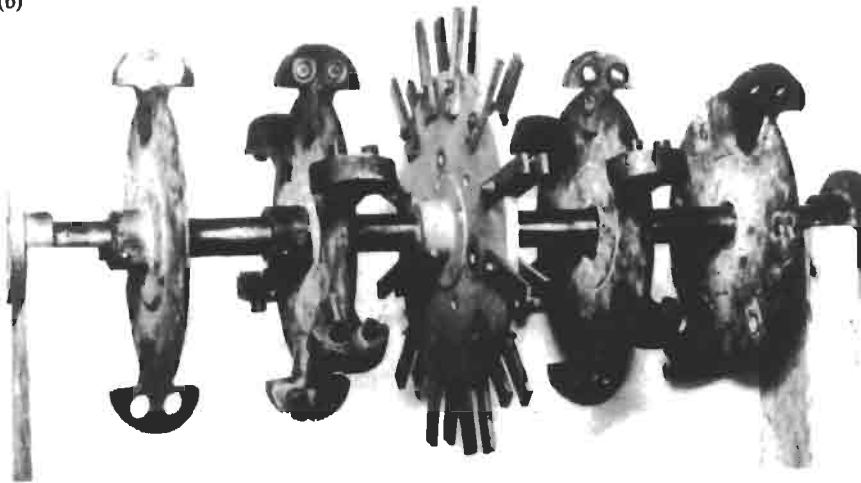


Fig. 19.3 (a) Distribution of corrosion on surfaces of rotating disc specimens and (b) assembly of specimens attached to rotating discs

water at high velocity was developed by the staff of the US Naval Engineering Experiment Station at Annapolis, Maryland³⁶. A typical assembly of discs and specimens is shown in Fig. 19.3b.

The action of the rotating discs with their attached specimens causes violent agitation of the liquid in the tank. Depending on the height of liquid above the specimens, as determined by the location of the overflow pipe, there may be considerable whipping of air bubbles into the liquid or none at all, as desired. The heat of agitation causes the temperature to rise. This may be controlled readily by adjusting the amount of fresh cold liquid, for example sea-water, allowed to pass into the tank and out through the overflow pipe. It is not difficult to hold the temperature within 1–2°C of the desired value.

The use of rotating discs to carry test specimens has been extended to studies of protective coatings in what are considered to be 'accelerated' tests of such coatings for service underwater³⁷.

Velocity effects involving a high differential in velocity between adjacent areas are achieved simply by exposing a test specimen to the action of a submerged jet. This sort of test has been very popular and very useful in studying impingement attack or erosion of condenser tube alloys. It was introduced originally by Bengough and May³⁸ and later modifications were described subsequently by May and Stacpoole³⁹. The appearances of typical specimens from this test are shown in Fig. 19.4. In this test the dimensions of test specimens should be standardised, since the depth of attack has been found to be influenced by the extent of the immersed area of the specimen that is outside the impingement zone.

Along the same general lines is an apparatus employed by Brownsdon and Bannister⁴⁰ in which a stream of air at high velocity is directed against the surface of a submerged test specimen (*see also p. 19:75*).

A straightforward way to study velocity effects is to force the testing liquid through tubular specimens, which may be arranged to form model piping systems for studying the peculiar corrosion that may result from severe turbulence effects downstream of valves, reducers, branch connections, elbows, and other fittings. In such systems the rates of flow can be measured by suitable orifice meters and regulated by control valves. A somewhat similar technique applied to condenser-tube alloys is to test them as installed in model tube-bundle assemblies⁴¹. Butler *et al.* have described a laboratory test rig for studying the effects of flowing water on steel pipework⁴².

Other methods involve holding specimens in suitable fixtures so that they form the walls of channels through which the test solution can be passed at controlled rates of flow. Such devices have been used at the Harbor Island Test Station in North Carolina primarily for studying the electrode potential and polarisation characteristics of metals and alloys, but they are also suitable for observing effects of velocity on corrosion. This is illustrated in Fig. 19.5 in which the specimen and Pt electrode are of the same size and are placed parallel to one another in the holder. When required potentials are measured by inserting a capillary through the hole in the Pt; it is then removed to avoid shielding effect.

Effects of velocity are sometimes aggravated by the presence of abrasive solids in suspension, which increases deterioration by straight mechanical



<i>Sample no.</i>	<i>Alloy</i>	<i>Mass loss after 1 000 h (g)</i>	<i>Penetration of impingement pit (% of cross-section)</i>	<i>Appearance</i>
A	Arsenical 70/30 brass	0.262	40	Deep pit opposite jet, surrounding area darkly stained
B	Arsenical Admiralty brass	0.422	44	Deep pit opposite jet
C	Arsenical aluminium brass	0.010	1	Very slightly attacked opposite jet
D	Cu 10Ni	0.026	<1	No measurable attack opposite jet
E	Cu-30Ni-1Fe 1Mn	0.019	<1	No measurable attack opposite jet
F	Cu-30Ni-2Fe 2Mn	0.014	<1	Very slight pitting attack beneath brown tubercles of corrosion products. Also pitting in areas next to sample holder. No measurable attack opposite jet
G	Cu-30Ni	0.061	9	Pitted opposite jet

Materials A I conform to BS 2871 and ASIM B111

Fig. 19.4 (top) Pattern of corrosion of jet-impingement test specimens and (bottom) sample test data and results

abrasion as well as accelerating corrosion by continually exposing fresh surfaces to attack. Such attack is especially serious with pumps, agitators and piping systems. Special apparatus has been designed to measure the performance of materials under such conditions, as described, for example, by Fontana⁴³.

Special devices have been used to study erosion-corrosion by boiler water moving at high velocity, and an example is the method used by Wagner, Decker and Marsh⁴⁴.

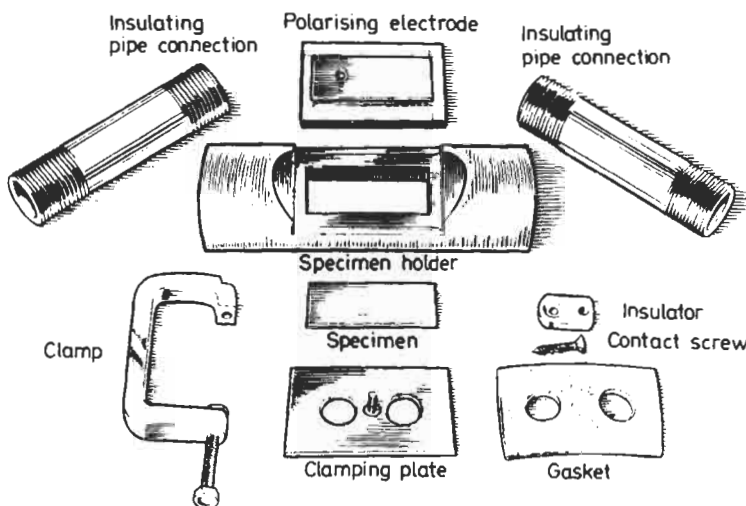


Fig. 19.5 Components of apparatus in which specimens form walls of channel for test solution

Where high rates of flow are desired with a small volume of testing liquid a specimen may be mounted in the form of a tube inside a large glass tube, and a small mass of liquid may be forced to flow through the restricted annular space between the two tubes. Such a method was used successfully in studying corrosion by milk where the volume of milk was small, the required movement being achieved simply by the use of an air lift to return the milk to an overhead reservoir from which it flowed by gravity through the test set up⁴⁵. Velocities as high as 0.6 m s^{-1} were studied in this way.

Volume of testing solution If exhaustion of corrosive constituents that may be present in minute concentrations and the accumulation of reaction products which may either accelerate or stifle further attack are to be avoided, the volume or mass of testing solution must be sufficiently large to avoid effects caused by these factors. In laboratory tests, however, practical considerations limit the volume of testing solution that can be provided for. A minimum of 250 ml of testing solution for each 6.3 cm^2 of specimen area is suggested in NACE TM0169-76.

Support of specimens Since crevices set up where specimens are in contact with their supports may become the seats of accelerated corrosion by concentration cell effects, special attention should be given to this detail in setting up tests. The area screened by the supporting members should be kept to a minimum, for example by making contact at a point or along a line rather than over any appreciable area. In some instances it may be desirable to apply some protective coating to the areas that are in contact with the supporting members. In any event, any corrosion that has occurred in the area of the supports should be taken into account in appraising and reporting the results of a test.

Somewhat along the same lines are techniques that have been employed to avoid edge effects by having the specimen come into contact only with

a pool of testing solution which does not cover its complete surface—as described, for example, by Brennert⁴⁶. A more elaborate technique in which the pool of testing solution was circulated by thermal currents was described by Smith⁴⁷.

Alternating-immersion Tests

One means of ensuring aeration of a testing solution in contact with a specimen is provided by an alternating-immersion corrosion test in which the specimen is alternately immersed in a solution and withdrawn from it in some predetermined cycle. This procedure also has the effect of allowing the test solution that clings to the specimen to become concentrated by evaporation while the specimen is out of the liquid, and in addition it permits corrosion products to remain and reach greater concentrations and undergo more chemical changes in immediate contact with the metal than can occur in continuous-immersion tests. In these ways, an alternating-immersion test may simulate certain circumstances of practical corrosion better than a continuous-immersion test and may, therefore, be preferred.

Since the conditions of this test can be standardised fairly readily, it has also been used as a routine test in comparing different alloys of the same general kind in the course of studies of effects of composition on properties, as, for example, in the researches by Hanawalt, Nelson and Peloubet on the corrosion of magnesium⁴⁸.

The ASTM have established a recommended procedure for alternating-immersion stress corrosion tests in 3·5% NaCl solution (ASTM G44:1988).

The alternating immersion may be accomplished either by moving specimens held in a suitable suspension rack into and out of containers holding the test solution, or by leaving the specimens fixed and raising and lowering the solution containers around them so as to immerse them or leave them suspended above the solution.

To favour reproducibility of results, the cycles of immersion and withdrawal must be kept the same from test to test. It is necessary to control the temperature and humidity of the atmosphere surrounding the test set-up as these affect the rate of evaporation of the solution and of drying of the specimens when they are out of the solution. It is also necessary to provide for replenishing losses of water from the test solution resulting from evaporation.

Water-line Tests

Materials may be subject to intense localised attack at the liquid level when they are partially immersed in a solution under conditions where the water line remains at a fixed position for long periods. This attack may be the result of concentration cell effects complicated by differences in the nature and adherence of corrosion-product films as they form in the water-line region as compared with those that form above or below this region.

The testing technique is very simple since it involves no more than providing means of supporting a specimen or specimens in a fixed position of

partial immersion, and of maintaining the liquid level constant by the continuous addition of distilled water to make up for evaporation losses. For maximum reproducibility of results, the dimensions of the specimens, and especially the ratio of areas above and below the liquid level, should be held constant, as should be the depth of immersion.

Heat-flux Effects

When heat flows into or out of a fluid through a containing wall, the wall surface reaches a temperature which differs from that of the bulk of the fluid. The wall's corrosion resistance at this temperature may be significantly different from its resistance at the bulk-fluid temperature. Tubes or tank walls heated by steam or direct flame have failed in service in which similar materials, not so heated, performed acceptably.

The name 'hot wall effect' was given to this phenomenon by Benedicks⁴⁹ who observed separation of dissolved gas from aerated water in boiler tubes. The metal wall was insulated from the cooler boiler water by the gas, its temperature rose substantially, and the more severe corrosion took the form of pitting. It was recognised subsequently that even without such gas formation, a hot-wall effect resulted when heat flowed through a wall into a fluid. The temperature difference which had to exist in order for heat to flow was increased by the insulating effect of the thin film of almost stagnant fluid at the wall surface. This film is thinned by rapid flow of a fluid through a tube, but is not eliminated at any finite velocity. Boiling of a liquid, by either bubble nucleation or coverage of the heating surface by a vapour film, increases the skin temperature further; the second mechanism provides much more severe insulation and greater temperature rise⁵⁰.

High rates of heat flow through heat-transfer surfaces in atomic energy installations studied by Groves caused him to develop an appropriate corrosion test method⁵¹. In this, a small sheet specimen in contact with a hot liquid, usually boiling, is heated externally so that its surface reaches the desired test temperature. The surface or skin temperature is close to the temperature at mid-thickness, which is measured by a thermocouple inserted in a drilled hole. The heating source is an electric soldering iron in which the tip is replaced by a flat-surfaced metal block. The voltage to the heat source is controlled by a variable transformer. Supplementary heating may be provided to the liquid in the test vessel by resistance-wire winding of the liquid container, or by an immersion heater (Fig. 19.6).

A similar unit, modified in details such as location of condenser, use of an agitator and shape of the vessel, was used by Fisher and Whitney⁵². Further substantial modifications to permit interface location of specimens, cooling of specimens and operation under applied pressure, have been described by Fisher⁵³. Earlier laboratory test methods tried by Fisher and Whitney⁵² included exposure of specimens heated by their own electrical resistance and of tubular specimens containing a pencil-type resistance-wire heater in a quartz tube.

To investigate corrosion in heated crevices filled with wetted paste a sandwich test assembly was designed by Gleekman and Swandby⁵² simulating

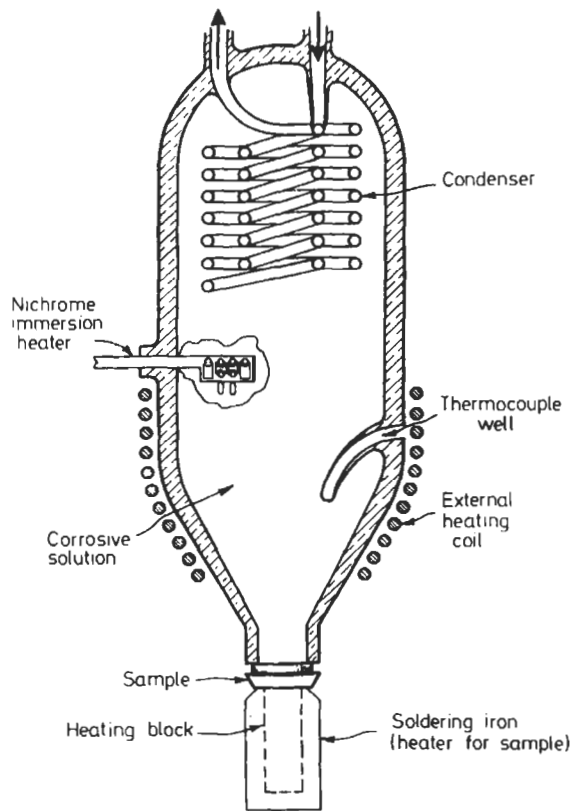


Fig. 19.6 Device for studying 'hot-wall' effects

a slotted cylindrical steam-heated drier. Two plates are bolted together, the lower being heated by an electric hot plate.

It has been concluded from data reported in these studies that the skin temperature is the major controlling factor in corrosion, not the rate of heat flow through the metal⁵². It has also been concluded, however, that corrosion rates at a given mid-specimen temperature do depend on the presence or absence of thermal flux⁵⁵. The difference between temperatures at skin and mid-specimen positions may account for this discrepancy.

Heat-flux corrosion rates can also be determined in plant tests using steam-heated tubular specimens which are weighed or callipered.

In addition to the direct effect of film temperature on corrosion rate, an indirect effect has been observed in the heating of some foods and chemicals, in which insulating solid corrosion films form on different metals. By raising the metal surface temperature, these films may, when pervious, lead to further corrosion.

Apparatus and procedures for testing the corrosion resistance of alloys in brines at temperatures up to 120–150°C are described by Hart⁵⁶.

Testing procedures for corrosion inhibitors in heat flux conditions are discussed below.

Composition of Testing Solution

Changes in corrosivity with time may be observed by exposing fresh specimens to a solution that has already been used for testing. Where such changes are known to occur, or are suspected, it will be necessary to arrange for replacement of the testing solution after appropriate intervals or replenishment of constituents that may be consumed in the corrosion processes.

Electrochemical Measurements

In view of the electrochemical nature of corrosion it is not surprising that measurements of the electrical properties of the interface metal/solution (electric double layer) are used extensively in fundamental studies of the mechanism of corrosion, in corrosion testing and in monitoring and control in service. In the context of this section electrical measurements in the laboratory are used to assess the corrosion behaviour of metals and alloys in service, and to avoid the more tedious and prolonged field testing. Determinations of the corrosion rate, susceptibility of a metal to bimetallic corrosion, pitting, intergranular attack, stress-corrosion cracking, etc. are examples of corrosion phenomena that are studied in the laboratory by means of electrochemical methods in order to anticipate behaviour in service.

Progress in this field has been made possible with increase in knowledge of the detailed mechanism of corrosion and by the developments that have taken place in instrumentation. The widespread use of potentiostatic control (Section 19.2) and the availability of a range of commercial potentiostats have given a tremendous impetus to electrochemical testing, and have perhaps led to the unfortunate belief that corrosion testing in the laboratory and in the field can be replaced completely by electrochemical measurements in the laboratory under conditions of controlled potential. Indeed, La Que⁵⁷ in 1969 was prompted to express concern about the proliferation of publications describing electrochemical techniques for corrosion testing, and to advise caution regarding the extrapolation of results obtained in the laboratory with a potentiostat to the performance of metals in service.

Although important contributions in the use of electrical measurements in testing have been made by numerous workers it is appropriate here to refer to the work of Stern and his co-workers^{58,59} who have developed the important concept of *linear polarisation*, which led to a rapid electrochemical method for determining corrosion rates, both in the laboratory and in plant. Pourbaix⁶⁰ and his co-workers on the basis of a purely thermodynamic approach to corrosion constructed potential-pH diagrams for the majority of metal-H₂O systems, and by means of a combined thermodynamic and kinetic approach developed a method of predicting the conditions under which a metal will (a) corrode uniformly, (b) pit, (c) passivate or (d) remain immune. Laboratory tests for crevice corrosion and pitting, in which electrochemical measurements are used, are discussed later.

Techniques

Electrochemical methods of testing involve the determination of specific properties of the electrical double layer formed when a metal is placed in contact with a solution (see Section 20.1), and these can be summarised as follows.

1. The potential difference across the electric double layer $\Delta\psi$. This cannot be determined in absolute terms but must be defined with reference to another charged interface, i.e. a reference electrode. In the case of a corroding metal the potential is the corrosion potential which arises from the mutual polarisation of the anodic and cathodic reactions constituting the overall corrosion reaction (see Section 1.4).
2. The reaction rate per unit area i . For a corroding metal the partial anodic and cathodic current densities cannot be determined directly by means of an ammeter unless the anodic and cathodic areas can be separated physically, e.g. as in a bimetallic couple. If the metal is polarised a *net* current i_c for cathodic polarisation, and i_a for anodic polarisation, will be obtained and can be measured by means of an ammeter.
3. The capacitance. The electrical double layer may be regarded as a resistance and capacitance in parallel (see Section 20.1), and measurements of the electrical impedance by the imposition of an alternating potential of known frequency can provide information on the nature of a surface. Electrochemical impedance spectroscopy is now well established as a powerful technique for investigating electrochemical and corrosion systems.

The most commonly used measurements are as follows:

1. Determination of the steady-state corrosion potential E_{corr} .
2. Determination of the variation of E_{corr} with time.
3. Determination of the $E - i$ relationships during polarisation at constant current density (galvanostatic) the potential being the variable.
4. Determination of the $E - i$ relationships during polarisation at constant potential (potentiostatic) the current being the variable.
5. Determination of the electrochemical impedance under alternating potential conditions as a function of frequency.
6. Determination of electrochemical noise: fluctuations of the free potential or fluctuations of the current when a constant potential is maintained.

Instruments

The techniques and instruments used may be classified as follows:

1. Potential measurements—a reference electrode and a potentiometer or electrometer which require only a small current to give a measurement of e.m.f. and thus minimise polarisation of the electrodes.
2. Current measurements—milliammeters or the measurements of the IR drop across a conductor of known resistance.

3. Galvanostatic polarisation—constant direct current power units, or banks of accumulators or dry cells used in conjunction with a variable resistance.
4. Potentiostatic polarisation—potentiostats with varying output currents.
5. Determination of impedance—a.c. bridges of various frequencies.

Impedance measurements, originally used in fundamental studies of anodic oxidation, have great power for deriving corrosion rates and information about reaction mechanisms for processes that occur at a corroding surface using readily available instrumentation. Armstrong *et al.*⁶¹ have used impedance measurements for studying the active-passive transition of chromium and Epelboin *et al.*⁶² describe its use for determining the instantaneous corrosion rate of a metal. Sathyahararyana⁶³ has described a method using Faradaic rectification to determine the instantaneous corrosion rate, in which no reference electrode is required; the electrodes consist of the metal under study and a counter electrode of a large area of the same metal. Macdonald⁶⁴ in a recent review of electrochemical impedance spectroscopy has highlighted the enormous advantage it offers over other electrochemical methods of being able to evaluate the validity of the data using the Kramers-Kronig transforms. While the use of impedance techniques is usually restricted to homogenous corrosion situations, applications to localised corrosion have been reported. These included pitting⁶⁵⁻⁶⁷ abrasion⁶⁸, other types of corrosion⁶⁹⁻⁷¹ and stress-corrosion cracking⁷².

The potentiostatic technique has a number of variations and the potential may be increased or decreased incrementally, changed continuously at a pre-determined rate (potential sweep) or applied as pulses of very short duration. The applications of the potentiostatic technique are considered in detail in Sections 1.4, 1.5 and 19.2, and will not be considered here.

The application of a stochastic approach to the study of pitting was pioneered by Sato⁷³. Shibata and Takeyama⁷⁴ then developed stochastic theory to study the statistical variation of the pitting potential determined by the potential sweep method. Subsequently, Williams and his co-workers⁷⁵⁻⁷⁷ described how electrochemical noise (current fluctuations in systems under potentiostatic control or potential fluctuations at the corrosion potential) can be analysed to provide information on the initiation and propagation of pitting corrosion on stainless steels. In a recent review Gabrielli *et al.*⁷⁸ discuss published results for both stable pitting, where statistical counting is the major technique of investigation, and unstable pitting during the pre-pitting stage, where the techniques that can be applied include statistical counting, ensemble averages and spectral analysis.

Electrochemical Cells

Since the single potential of a metal cannot be measured it is necessary to use a suitable reference electrode such as the Hg/Hg₂Cl₂/KCl electrode or the Ag/AgCl/KCl electrode, and although potentials are frequently expressed with reference to the standard hydrogen electrode (S.H.E.) the use of this electrode in practice is confined to fundamental studies rather than testing.

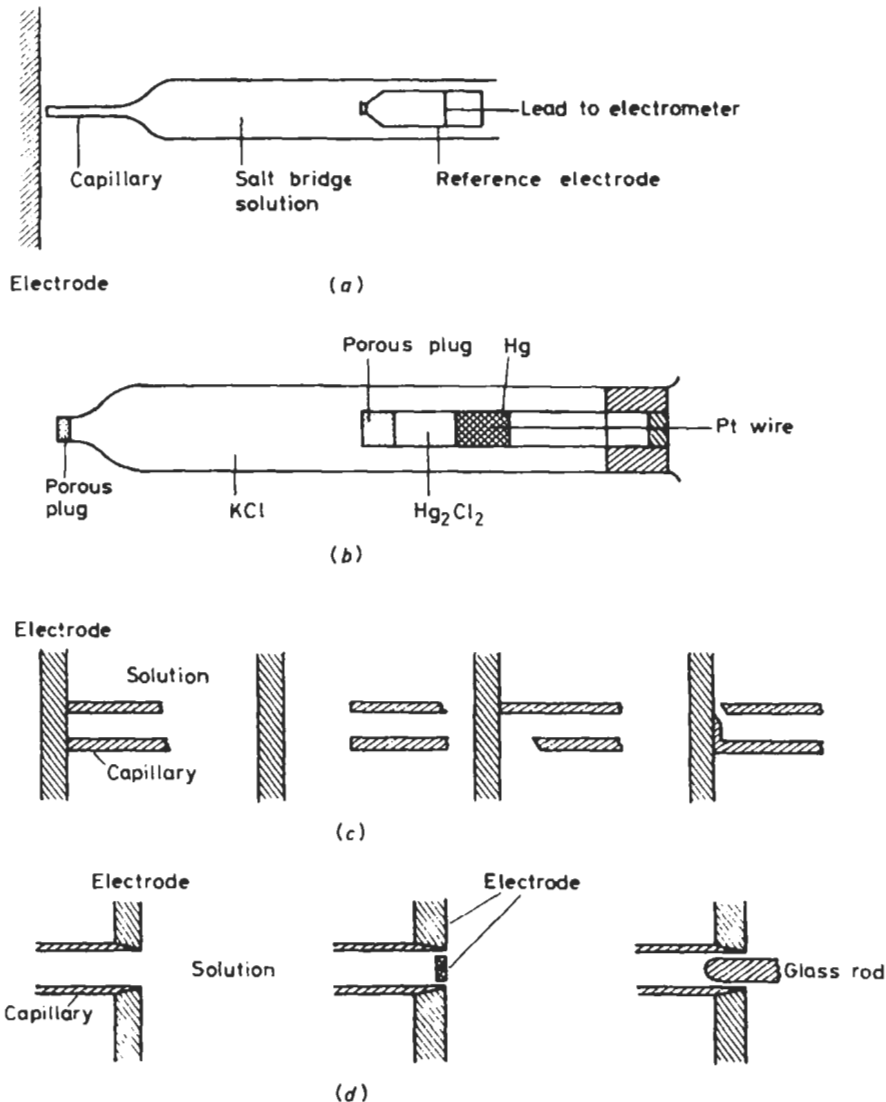


Fig. 19.7 Reference electrodes and capillaries. (a) Reference electrode, salt bridge and Luggin capillary; (b) calomel electrode; (c) frontal types of capillaries and positions; (d) rearside capillaries (after von Fraunhofer and Banks⁹⁰)

Details of the preparation of reference electrodes, salt bridges, capillaries, etc. are given in the book by Ives and Janz⁷⁹ and elsewhere⁸⁰⁻⁸³.

Measurements of the corrosion potential of a single metal corroding uniformly do not involve an IR drop, but similar considerations do not apply when the metal is polarised by an external c.m.f., and under these circumstances the IR drop must be minimised by using a Luggin capillary placed close to the surface of the electrode (see Fig. 1.22, Section 1.4). Even so, the IR drop is not completely eliminated by this method, and a further error is introduced by the capillary shielding the surface from the current flow

with a consequent decrease in c.d. At high c.d. this error due to the IR drop can conceal the Tafel region by distorting the measured overpotentials, a difficulty that can be overcome by determining the resistance of the solution at the capillary tip and by making an appropriate correction for each value of the current density. Alternatively, electronic feedback circuits may be employed for automatic compensation of the IR drop, and this method is attractive if rapid variations in overpotential are being studied⁸⁴⁻⁸⁷. Other methods are by using a Piontelli capillary^{88,89} or a rearside capillary⁹⁰. (Fig. 19.7). However, in testing in electrolyte solutions of low resistivity these errors are normally small, and the conventional Luggin capillary is used in conjunction with a salt bridge and reference electrode.

For polarisation studies the cell must make provision for the metal electrode under study, an auxiliary or counter electrode, and a Luggin capillary. Provision must also be made for introducing a gas such as oxygen-free nitrogen or argon, which serves to remove dissolved oxygen and to prevent its introduction during the test (or to introduce it if required at predetermined partial pressures) and to agitate the solution; additional agitation if required can be obtained by means of a stirrer (electric or magnetic).

Figure 19.8 shows the design of an all-glass cell, which has been listed as the standard polarisation cell in the ASTM Recommended Practice G5:1987, which makes provision for the essential requirements listed above; this cell is typical of those used for fundamental studies and for testing, although details of design may vary.

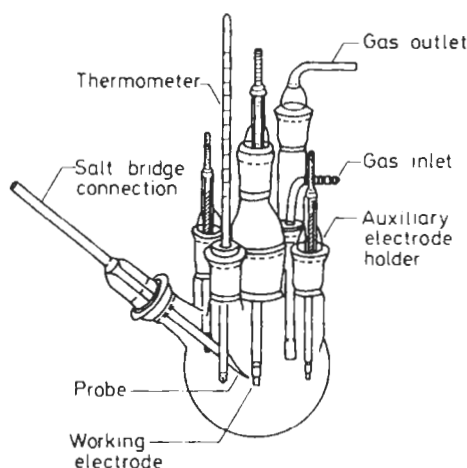


Fig. 19.8 All-glass cell for studies of polarisation of metal electrodes (after ASTM G5:1987)

The metal electrode to be studied must be carefully prepared, attached to an electrical lead and mounted so that a known surface area of one face is presented to the solution. Several procedures are used such as mounting in a cold setting resin (Araldite) or inserting into a close-fitting holder of p.t.f.e. In the case of metal-solution systems that have a propensity for pitting care must be taken to avoid a crevice at the interface between metal specimen and the mounting material, and this can be achieved effectively by mounting the

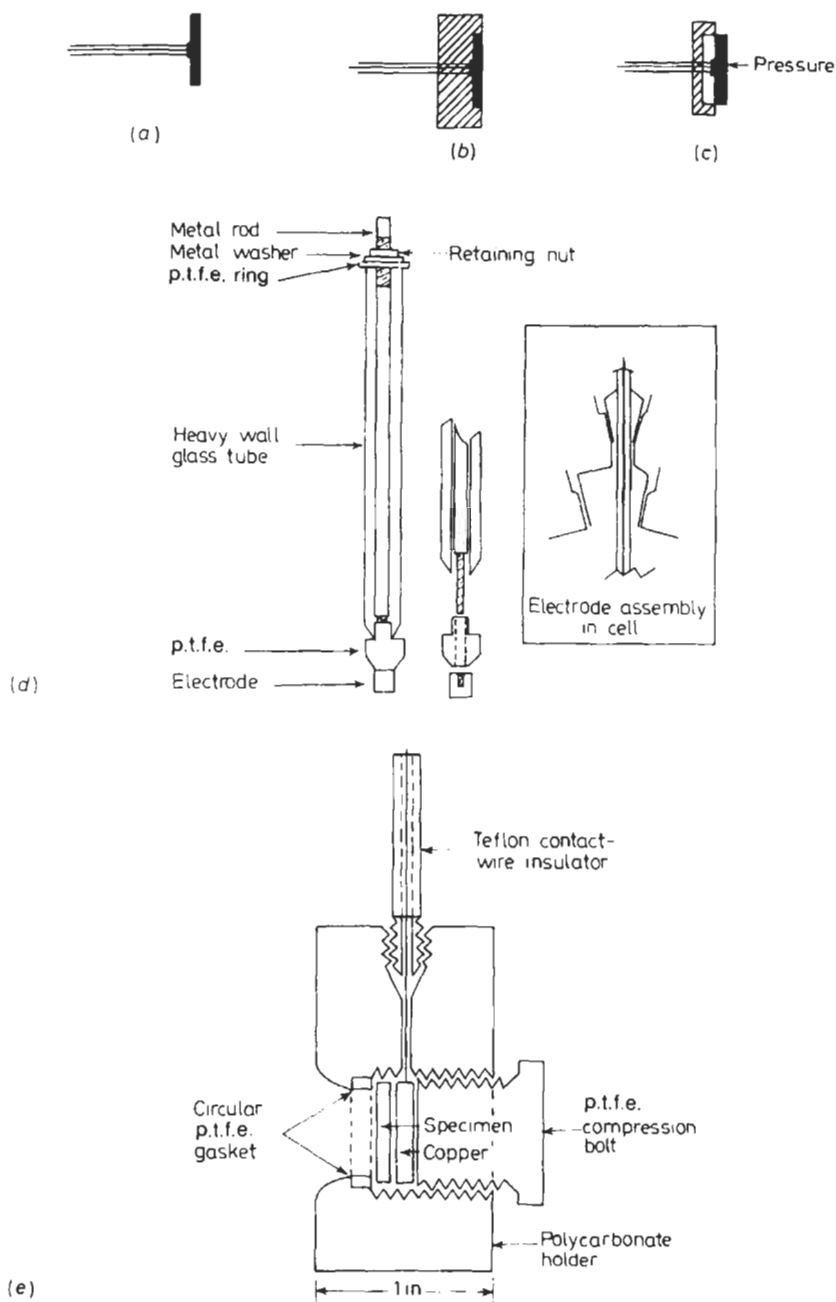


Fig. 19.9 Methods of mounting specimens. (a) Wire soldered to metal specimen, wire being enclosed in glass tube; (b) specimen completely encapsulated in cold-setting resin and resin ground down to expose one face; (c) specimen clipped into machined p.t.f.e. holder; (d) Stern-Makrides⁹¹ pressure gasket for cylindrical specimen; (e) pressure gasket for sheet or foil⁹⁵

specimen in a cold-setting resin with approximately 1 mm thickness on the working face; the latter is then removed by carefully abrading on emery paper to expose the specimen. In view of the widespread use of the cell shown in Fig. 19.8 suitable electrode holders, based on the use of a compression gasket of p.t.f.e. or a similar inert polymer, have been designed for bulk metal specimens^{91,92}, wires⁹³, tubes⁹⁴, sheets and foil⁹⁵ and for high-temperature high-pressure assemblies⁹⁶. Examples of methods of mounting specimens to give a defined area of surface are shown in Fig. 19.9⁹⁰.

Various types of reference electrodes have been considered in Section 20.3, and the potentials of these electrodes and their variation with the activity of the electrolyte are listed in Table 21.7, Chapter 21. It is appropriate, however to point out here that the saturated calomel electrode (S.C.E.), the silver-silver chloride electrode and the copper-copper sulphate electrode are the most widely used in corrosion testing and monitoring.

To avoid contamination of the solution under study, and to minimise the liquid-junction potential, it is usual to use a salt bridge, but in many cases this can be dispensed with; thus if corrosion in a chloride-containing solution is being studied a Ag/AgCl electrode immersed directly in the solution could be used; similarly a Pb/PbO₂ electrode could be used for studies of corrosion in H₂SO₄.

Measurements of the Corrosion Potential

The significance of the corrosion potential in relation to the equilibrium potentials and kinetics of anodic and cathodic reactions has been considered in Section 1.4, but it is appropriate here to give some examples of its use in corrosion testing. Pourbaix⁶⁰ has provided a survey of potential measurements in relation to the thermodynamics and kinetics of corrosion, and an example of how they can be used to assess the pitting propensity of copper in Brussels water is given in Section 1.6.

The determination of the corrosion potential of the two metals constituting a bimetallic couple will provide information on which one of the two will be predominantly anodic and will suffer enhanced corrosion when they are coupled. Similarly the effect of microscopical heterogeneities in alloys on corrosion has been investigated by measuring the corrosion potentials of selected small areas of the surface of the metal. Smith and Pingel⁹⁷ coated the surface of the metal with a lacquer of ethyl cellulose (deposited from a volatile solvent), allowed it to dry and then perforated selected areas with a micro-hardness tester using a steel stylus ground to a truncated cone, and Budd and Booth⁹⁸ using a similar technique were able to produce punctures in the film down to 35 μm diameter. Microelectrodes for potential measurements were described by Cleary⁹⁹ who used a Ag/AgCl/Cl⁻ electrode with capillary tips down to 15 μm ; Cleary also described micro-glass electrodes of approximately 30 μm diameter for the determination of pH. More recently, Doig and Edington¹⁰⁰ used microelectrodes with an internal diameter at the tip of about 0.2 μm to measure localised corrosion potentials in the grain boundary regions of aged Al-Mg and Al-Cu alloys, and Davis¹⁰¹ used microelectrodes with a tip diameter of 1 μm to measure pH during stress corrosion of aluminium alloys.

Potential-time relationships have been widely used for studying film formation and film breakdown, as indicated by an increase or decrease in the corrosion potential, respectively. May¹⁰² studied the corrosion of 70/30 brass and aluminium brass in sea-water and showed how scratching the surface resulted in a sudden fall in potential to a more negative value followed by a rapid rise due to re-formation of the film; conversely, the pitting of stainless steel in chemical plant may be detected by a sudden decrease in potential¹⁰³.

Hoar and his co-workers^{104, 105} used potential changes to study film breakdown and repair during the stress-corrosion cracking of austenitic stainless steels in boiling saturated MgCl_2 solution. More recently, Horst, *et al.*¹⁰⁶ have used potential measurements as a test to predict the stress-corrosion susceptibility of 2219 aluminium alloy products (alloys containing approximately 6% Cu and tempered to give maximum strength and resistance to stress-corrosion cracking). The test solution used was methanol plus carbon tetrachloride and, it was shown that susceptible alloys were 200–500 mV more positive than non-susceptible alloys, and that this difference in potential was revealed in less than 1 h. They claim that the test is more sensitive than that in which sodium chloride plus hydrogen peroxide is used as the test solution, since the latter gives potential differences of only 20 mV.

A detailed and well-referenced account of electrochemical methods of testing has been written by Dean, France and Ketcham in a section of the book by Ailor². ASTM G5:1987 outlines standard methods for making potentiostatic and potentiodynamic anodic polarisation measurements and ASTM G3:1974 (R1981) gives conventions applicable to electrochemical measurements in corrosion testing.

Polarisation Resistance

It is evident from previous considerations (see Section 1.4) that the corrosion potential E_{corr} provides no information on the corrosion rate, and it is also evident that in the case of a corroding metal in which the anodic and cathodic sites are inseparable (*c.f.* bimetallic corrosion) it is not possible to determine i_{corr} by means of an ammeter. The conventional method of determining corrosion rates by mass-loss determinations is tedious and over the years attention has been directed to the possibility of using instantaneous electrochemical methods. Thus based on the Pearson derivation¹⁰⁷, Schwerdtfeger, *et al.*^{108, 109} have examined the logarithmic polarisation curves for 'potential breaks' that can be used to evaluate the corrosion rate; however, the method has not found general acceptance.

Skold and Larson¹¹⁰ in studies of the corrosion of steel and cast iron in natural water found that a linear relationship existed between potential and the applied anodic and cathodic current densities, providing the values of the latter were low. However, the recognition of the importance of these observations is due to Stern and his co-workers^{58, 59} who used the term 'linear polarisation' to describe the linearity of the $\eta - i$ curve in the region of E_{corr} , the corrosion potential. The slope of this linear curve, $\Delta E - \Delta i$ or $\Delta E - \Delta i$, is termed the *polarisation resistance*, R_p , since it has dimensions of ohms, and this term is synonymous with 'linear polarisation' in

describing the 'Stern-Geary' technique for evaluating corrosion rates.

Stern and Geary^{58,59} on the basis of a detailed analysis of the polarisation curves of the anodic and cathodic reactions involved in the corrosion of a metal, and on the assumption that both reactions were charge-transfer controlled (transport overpotential negligible) and that the iR drop involved in determining the potential was negligible, derived the expression

$$\frac{1}{R_p} = \left(\frac{\Delta i}{\Delta E} \right)_{E_{\text{corr.}}} = 2.3 \left(\frac{b_a + |b_c|}{b_a |b_c|} \right) i_{\text{corr.}} \quad \dots (19.1)$$

where R_p is the polarisation resistance determined at potentials close to $E_{\text{corr.}}$, and b_a, b_c are the Tafel constants; note that in the case of b_c the negative sign is disregarded. This equation shows that the corrosion rate is inversely proportional to R_p (or directly proportional to the reciprocal slope of the $\Delta E - \Delta i$ curve) at potentials close to $E_{\text{corr.}}$ ($\gtrsim 10$ mV), and at that $i_{\text{corr.}}$ can be evaluated providing the Tafel constants are known. For a process that is controlled by diffusion of the cathode reactant (transport control) and in which the anodic process is under activation control a similar linear relationship applies:

$$\frac{1}{R_p} = \left(\frac{\Delta i}{\Delta E} \right)_{E_{\text{corr.}}} = \frac{2.3 i_L}{b_a} = \frac{2.3 i_{\text{corr.}}}{b_a} \quad \dots (19.2)$$

where i_L is the limiting current density of the cathodic reaction and it is assumed that $i_L = i_{\text{corr.}}$.

Stern and Weisert¹¹¹ by taking arbitrary values of the Tafel constants showed that corrosion rates determined by the polarisation resistance techniques are in good agreement with corrosion rates obtained by mass loss methods.

The importance of the method in corrosion testing and research has stimulated other work, and since Stern's papers appeared there have been a number of publications many of which question the validity of the concept of linear polarisation. The derivation of linearity polarisation is based on an approximation involving the difference of two exponential terms, and a number of papers have appeared that have attempted to define the range of validity of polarisation resistance measurements. Barnartt^{112,113} derived an analytical expression for the deviations from linearity and concluded that it varied widely between different systems. Leroy¹¹⁴, using mathematical and graphical methods, concluded that linearity was sufficient for the technique to be valid in many practical corrosion systems. Most authors emphasise the importance of making polarisation resistance measurements at both positive and negative overpotentials.

Oldham and Mansfeld¹¹⁵ approached the problem of linearity in a different way and their derivation avoids the approximation used by Stern and Geary. They conclude that although linearity is frequently achieved this is due to three possible causes: (a) ohmic control due to the IR drop rather than control according to linear polarisation, (b) the similarity of the values of b_a and b_c and (c) a predisposition by the experimenter to assume that the $\Delta E - \Delta i$ curves near $E_{\text{corr.}}$ must be linear. In a later paper Oldham and Mansfeld¹¹⁶ showed that linearity of the $\Delta E - \Delta i$ curve is not essential and

that i_{corr} can be evaluated from the slopes of the tangents of the non-linear curve determined at potentials of about 20–30 mV more positive and negative than E_{corr} .

Hickling¹¹⁷, in attempting to study the corrosion of steels under thin film conditions that simulate atmospheric exposure, took into account the time-dependence of polarisation measurements, and developed a technique using galvanostatic transients.

Tafel Constants

It is evident from equations 19.1 and 19.2 that the evaluation of i_{corr} from R_p determinations requires a knowledge of the Tafel constants b_a and b_c , which may not be available for the system under study and which may change in value during the progress of the determination. The determination of the Tafel constants from complete $\eta - i$ curves for each system studied is time consuming, and may not be particularly accurate owing to resistance and mass transfer effects. Hoar¹¹⁸ has criticised the method on these grounds and has pointed out that the complete Tafel equations for the anodic and cathodic reactions, which have to be determined to evaluate the Tafel slopes, can be used to calculate i_{corr} without resorting to the polarisation resistance technique (see Section 1.4). Mansfeld^{119–122} suggests that polarisation curves obtained in the R_p region can be fitted to various theoretical curves, preferably by computer analysis, to give the separate value of both b_a and b_c , which since they are determined simultaneously with the R_p values avoids the criticism that they may change substantially during the corrosion test (see p. 19:40).

The controversy that arises owing to the uncertainty of the exact values of b_a and b_c and their variation with environmental conditions, partial control of the anodic reaction by transport, etc. may be avoided by substituting an empirical constant for $(b_a + |b_c|/b_a|b_c|)$ in equation 19.1, which is evaluated by the conventional mass-loss method. This approach has been used by Makrides¹²³ who monitors the polarisation resistance continuously, and then uses a single mass-loss determination at the end of the test to obtain the constant. Once the constant has been determined it can be used throughout the tests, providing that there is no significant change in the nature of the solution that would lead to markedly different values of the Tafel constants.

Applications

The method in spite of its limitations has a number of significant advantages and provides a method of rapidly monitoring the instantaneous corrosion rates; furthermore, it has the advantage that the small changes in potential required in the determination do not disturb the system significantly. It is capable of measuring both high and low corrosion rates with accuracy, and may be used as a laboratory tool for testing or research, or for monitoring corrosion rates of plant (see Section 19.3).

Stern⁵⁹ pointed out that the polarisation resistance method could be of value for determining the effect of changes of environment (composition, temperature, velocity) and alloy composition on the corrosion rate and for evaluating inhibitors, and since his original publications the method has been widely used for a variety of studies. Thus Legault and Walker¹²⁴ used the method for studying the inhibition of the corrosion of steel in chloride solutions by NaNO_2 , and France and Walker¹²⁵ extended this approach to a study of the *in situ* corrosion of the various metals in automotive-engine cooling systems. Jones and Grèene¹²⁶ developed the theory of transient linear polarisation to study very low corrosion rates, such as occur with surgical implant materials, and have shown how polarisation resistance data can be used to monitor the onset of pitting or other forms of localised corrosion.

Wilde¹²⁷ has applied the Jones d.c.-bridge technique¹²⁸ to compensate for errors due to the *IR* drop, and has obtained meaningful corrosion rates from polarisation resistance data in high-temperature high-purity water in nuclear reactors.

Bureau¹²⁹ and others¹³⁰ have tried to apply the technique for evaluating the corrosion rate of painted metals, and although the results are controversial the method has also been used successfully in the study of canning materials and lacquered surfaces¹³¹⁻¹³³.

Rowlands and Bentley¹³⁴ have provided an account of the possibilities for continuously monitoring corrosion rates by polarisation resistance measurements, and they also describe the development of a commercial instrument, which uses low-frequency square-wave current to polarise the test specimens.

Derivation of Linear Polarisation Method for Determining Corrosion Rates

It is assumed that

1. The corrosion current i_{corr} (it is also assumed that the area of the metal is 1 cm^2 so that $I_{\text{corr}} = i_{\text{corr}}$) occurs at a value within the Tafel region for the anodic and cathodic reaction, i.e. transport overpotential is negligible.
2. E_{corr} is remote from the reversible potentials of the anodic and cathodic reactions.
3. The *IR* drop in measuring the polarised potential is negligible.

Following Oldham and Mansfeld¹¹⁵, but using the symbols that have been adopted in the present work, it is required to show that*

$$\left(\frac{di}{dE} \right)_{E_{\text{corr}}} Z = i_{\text{corr}} \left[\frac{1}{b_a} + \frac{1}{b_c} \right] \quad \dots (19.3)$$

where b_a , b_c are the Tafel slopes of anodic and cathodic reactions constituting the overall corrosion reaction, i.e. i_{corr} is linearly related to the

* Note that the inclusion of the factor 2.3 (see equation 19.1) for converting $\ln b$ to $\log b$ is not necessary for this proof.

polarisation resistance (dE/di) at potentials close to E_{corr} .

At any potential E the net current is given by

$$i = i_1^- - |i_1^+| + i_2^- - |i_2^+| \quad \dots(19.4)$$

where i_1^- is the anodic current for metal dissolution and i_1^+ is the reverse cathodic current, and i_2^- is the cathodic current for reduction of the cathode reactant (dissolved O_2 , H_3O^+ , H_2O , etc.) and i_2^+ the reverse current.

The rate of the anodic reaction at a potential E is given by

$$i_1^- = i_{0,1} \exp \left\{ \frac{E - E_{r,1}}{b_a} \right\} \quad \dots(19.5)$$

where $E_{r,1}$ is the reversible potential for the anodic dissolution reaction, b_a is the Tafel slope and $i_{0,1}$ is the exchange current density. Similarly for the cathodic reaction

$$|i_2^+| = i_{0,1} \exp \left\{ \frac{E_{r,2} - E}{b_c} \right\} \quad \dots(19.6)$$

Similar expressions may be written for the partial reverse rates $|i_1^+|$ and i_2^- , but under the conditions assumed here they may be neglected. Hence substituting equations 19.5 and 19.6 in equation 19.4.

$$i = i_{0,1} \exp \left\{ \frac{E - E_{r,1}}{b_a} \right\} - i_{0,2} \exp \left\{ \frac{E_{r,2} - E}{b_c} \right\} \quad \dots(19.7)$$

At the corrosion potential E_{corr} , the *net* current i becomes zero, since $i_1^- = |i_2^+|$. Thus the two terms on the right-hand side of equation 19.7 become equal to one another and equal to i_{corr} , the corrosion density. Thus, replacing E in equation 19.7 by E_{corr} gives

$$i_{\text{corr}} = i_{0,1} \exp \left\{ \frac{E_{\text{corr}} - E_{r,1}}{b_a} \right\} = i_{0,2} \exp \left\{ \frac{E_{r,2} - E_{\text{corr}}}{b_c} \right\} \quad \dots(19.8)$$

Differentiating equation 19.7 with respect to E gives

$$\frac{di}{dE} = \frac{i_{0,1}}{b_a} \exp \left\{ \frac{E - E_{r,1}}{b_a} \right\} + \frac{i_{0,2}}{b_c} \exp \left\{ \frac{E_{r,2} - E}{b_c} \right\} \quad \dots(19.9)$$

which for $E = E_{\text{corr}}$ becomes

$$\left(\frac{di}{dE} \right)_{E_{\text{corr}}} = \frac{i_{0,1}}{b_a} \exp \left\{ \frac{E_{\text{corr}} - E_{r,1}}{b_a} \right\} + \frac{i_{0,2}}{b_c} \exp \left\{ \frac{E_{r,2} - E_{\text{corr}}}{b_c} \right\} \quad \dots(19.10)$$

Combining equations 19.8 and 19.10 gives equation 19.3 the Stern Geary equation by simple algebra. However, Oldham and Mansfield point out that further differentiation of equation 19.9 gives

$$\frac{d^2i}{dE^2} = \frac{i_{0,1}}{b_a^2} \exp \left\{ \frac{E - E_{r,1}}{b_a} \right\} - \frac{i_{0,2}}{b_c^2} \exp \left\{ \frac{E_{r,2} - E}{b_c} \right\} \quad \dots(19.11)$$

an equation which demonstrates that there is only one point (a point of inflection, corresponding to a minimum slope) at which the $di-dE$ curve has no curvature and is linear. It follows that

$$\left(\frac{d^2i}{dE^2}\right)_{E_{\text{corr}}} = \frac{i_{0,1}}{b_a^2} \exp\left\{\frac{E_{\text{corr.}} - E_{r,1}}{b_a}\right\} - \frac{i_{0,2}}{b_c^2} \exp\left\{\frac{E_{r,2} - E_{\text{corr.}}}{b_c}\right\} \quad \dots(19.12)$$

and combining this equation with equation 19.8 gives

$$\left(\frac{d^2i}{dE^2}\right)_{E_{\text{corr}}} = i_{\text{corr}} \left[\frac{1}{b_a^2} - \frac{1}{b_c^2} \right] \quad \dots(19.13)$$

For the $E - i$ plot to be linear at $E \approx E_{\text{corr.}}$

$$\left(\frac{d^2i}{dE^2}\right)_{E_{\text{corr.}}}$$

must be zero, but equation 19.13 shows that this will be true only if $b_a = b_c$.

Simultaneous Determination of Tafel Slopes and Corrosion Rates from R_p Determinations

Mansfeld¹²² points out that a major limitation of the polarisation resistance is that the factor $b_a b_c / 2 \cdot 3 (b_a + b_c)$ must be determined in order to evaluate $I_{\text{corr.}}$, and has devised a procedure in which this can be achieved by a graphical method.

The Stern-Geary equation can be written in the form

$$I_{\text{corr.}} = \frac{b_a b_c}{2 \cdot 3 (b_a + b_c)} \times \frac{1}{R_p} = \frac{B}{R_p} \quad \dots(19.14)$$

where $B = b_a b_c / 2 \cdot 3 (b_a + b_c)$ and $R_p = (dE/dI)_{E_{\text{corr.}}}$. Equation 19.14 is valid only if the relationship between I and E can be expressed as

$$I = I_{\text{corr.}} \left\{ \exp\left(\frac{2 \cdot 3 (E - E_{\text{corr.}})}{b_a}\right) - \exp\left(\frac{-2 \cdot 3 (E - E_{\text{corr.}})}{b_c}\right) \right\} \quad \dots(19.15)$$

Combining equations 19.14 and 19.15 and rearranging gives

$$2 \cdot 3 R_p I = \frac{b_a b_c}{b_a + b_c} \left\{ \exp\left(\frac{2 \cdot 3 \Delta E}{b_a}\right) - \exp\left(-\frac{2 \cdot 3 \Delta E}{b_c}\right) \right\} \quad \dots(19.16)$$

where $\Delta E = E - E_{\text{corr.}}$. Since the right-hand side of equation 19.16 depends only upon the Tafel slopes it should be possible to evaluate b_a and b_c from plots of $R_p I$ vs. ΔE .

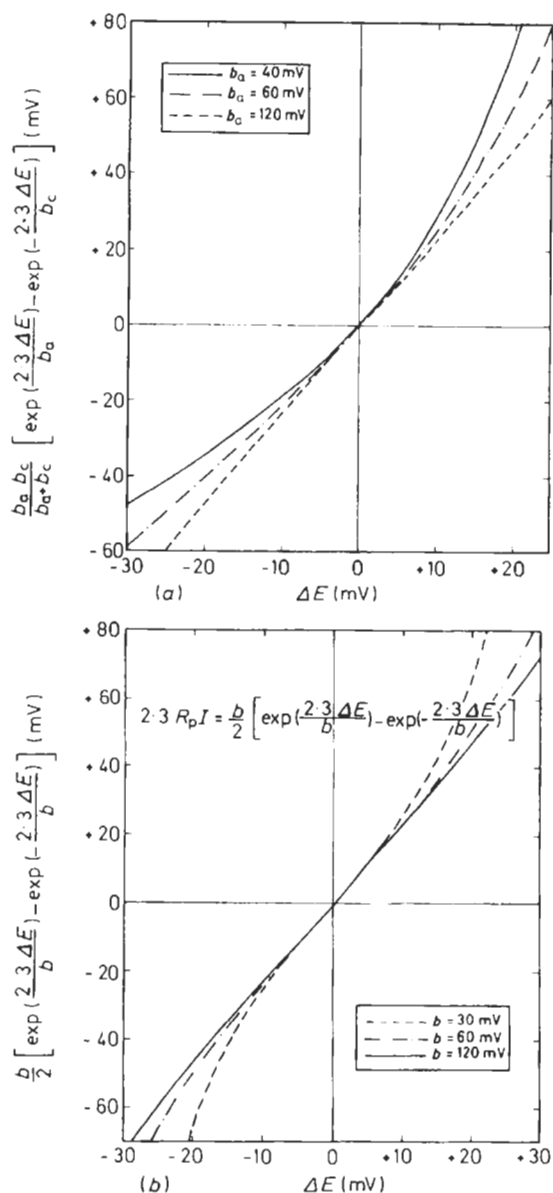


Fig. 19.10 Plots of the right-hand side of equation 19.16 vs. $\Delta E = E - E_{\text{corr.}}$ for various combinations of Tafel slopes. (a) b_c constant at 120 mV, b_a varied, and (b) $b_a = b_c = b$ (after Mansfeld¹²²)

Figure 19.10a shows a theoretical plot of the right-hand side of equation 19.16 vs. ΔE in which the cathodic Tafel slope has been assumed to be constant at 120 mV and the anodic Tafel slope to have the arbitrary slopes of 40, 60 and 120 mV. It can be seen that linearity over a range of positive and negative potentials ΔE is achieved only when $b_a = b_c$ and that linearity is confined to $\Delta E \approx 0$ when b_a and b_c differ.

In Fig. 19.10*b* it has been assumed that the Tafel slopes are equal, i.e. $b_a = b_c = b$ and the modified expression for the right-hand side of equation 19.16 has been plotted against ΔE for different values of b (30, 60 and 120 mV). Comparison of Fig. 19.10*a* and 19.10*b* shows how the curvature of the plots differs at cathodic potentials, i.e. $\Delta E < 0$. Thus the kinetic behaviour of a corroding metal, as expressed by different combinations of Tafel slopes, can be organised by this method of plotting curves. This theoretical approach has been confirmed experimentally by Mansfeld for the system Fe/H₂SO₄.

Mansfeld points out that I_{corr} can be calculated from the measured polarisation curve by the following four steps which are based on equations 19.14 and 19.15.

1. Determine R_p from

$$\left(\frac{dI}{dE} \right)_{E_{\text{corr}}} = R_p^{-1}$$

by drawing a tangent at $\Delta E = 0$ i.e. at E_{corr} .

2. Multiply the current I measured at a certain value of ΔE by $2.3 R_p$ and plot $2.3 R_p I$ vs. ΔE for various values.
3. Determine from this plot the Tafel slopes b_a and b_c by curve fitting using the theoretical curves calculated for various values of b_a and b_c .
4. Calculate I_{corr} from equation 19.14 using the R_p value evaluated in Step 1 and the Tafel slopes determined in Step 3.

Tests for Bimetallic Corrosion

The extent of galvanic effects will be influenced by, in addition to the usual factors that affect corrosion of a single metal, the potential relationships of the metals involved, their polarisation characteristics, the relative areas of anode and cathode, and the internal and external resistances in the galvanic circuit (see Section 1.7).

The results of a galvanic corrosion test on a small scale are as a general rule no more than semi-quantitative. A principal reason for this is that the magnitude of the galvanic effect is a function of galvanic current density which is usually determined by the relative areas of the metals forming the couple. There may also be major differences in circuit resistances in tests as compared with practice—especially if current-measuring shunts of substantial resistance are made part of the circuit in the test. The geometric relationship between the metals in the test will also influence the result through effects on electrolyte resistance and the distribution of the galvanic currents.

The simplest procedure in studying galvanic corrosion is a measurement of the open-circuit potential difference between the metals in a couple in the environment under consideration. This will at least indicate the probable direction of any galvanic effect although no information is provided on the rate. A better procedure is to make similar open-circuit potential measurements between the individual metals and some appropriate reference electrode, which will yield the same information and will also permit obser-

variations of any changes in potential of the individual metals with time that will affect the overall potential difference in the couple. For most practical laboratory testing, the saturated calomel half cell is most convenient. The precision of the determinations is adequate and it is easy to maintain a constant concentration of potassium chloride.

The preferred potential-measuring instruments are potentiometers or electrometers, either of which permit measurements to be made without flow of sufficient current to polarise the electrodes during the determinations. It is also possible to use millivoltmeters if the internal resistance of the instrument is high enough to avoid any appreciable flow of current.

Open-circuit potential measurements do not indicate the all-important effects of continued current flow, and much more information is derived from frequent or continuous determinations of the magnitude of the galvanic current. In making these measurements it is necessary to avoid the use of instruments that will introduce sufficient resistance to exert a controlling effect on the magnitude of the galvanic current being measured. Instruments (zero-resistance ammeters) are available that permit current measurements to be made with zero resistance in the measuring circuit.² This may also be achieved by connecting the two metals to the input of a potentiostat and setting the control potential to zero volts; the output current of the potentiostat will then be equivalent to the galvanic current flowing between the two metals.

In many cases it will suffice to include in the circuit a shunt of appropriately low resistance over which IR -drop potential measurements can be made for ready calculation of the magnitude of the current flow. This technique permits measurements to be made as required without opening the circuit even momentarily for the introduction of current-measuring devices. It is also possible to arrange instruments in a circuit so that no measuring resistance is introduced in the galvanic current circuit¹³⁵.

An obvious method for studying galvanic corrosion either with or without supplementary electrical measurements is to compare the extent of corrosion of coupled and uncoupled specimens exposed under identical conditions. Such measurements may use the same techniques for estimating corrosion damage, such as mass-loss determinations, as have been described in connection with ordinary corrosion tests.

A convenient method of carrying out such a galvanic test in the laboratory has been described by Wesley¹³⁶ in which the vertical circular-path machine is used. Each assembly includes two pairs of dissimilar metals—one pair coupled galvanically while the other pair is left uncoupled in order to determine the normal corrosion rates under the same environmental conditions. The type of motion provided (specimens moving in a vertical circular path) enables electrical connections to be made without mercury cup or commutator and the leads can be connected to a calibrated resistance for current measurements attached to the specimen carrier.

It is often of interest also to measure both the external and internal resistances of the galvanic circuit by the use of appropriate resistance-measurement bridges or by even more elaborate techniques such as have been described by Pearson¹⁰⁷.

It is often desirable to know something about the probable distribution of galvanic effects in a galvanic couple. This will be determined, of course,

by the size and shape of the different metals and how they are placed relative to each other—whether more or less parallel in the electrolyte, close together or far apart, or joined along some line of contact. The distribution from such a line of contact may be observed directly if the test couples are exposed in this way and for long enough for sufficient corrosion to occur for it to be observed and measured. Alternatively, the distribution of the galvanic currents in terms of the current density on different portions of both the anode and cathode surfaces may be estimated from data derived from surveys of the potential field in the electrolyte around the couple. Such a potential survey may be made using a fixed and a movable reference electrode so that equipotential lines in several planes may be measured and plotted as was done by Copson¹³⁷ using a technique originally proposed by Hoar. By laborious analysis of the data from the potential surveys, it is possible to calculate the current distribution over different areas near to and remote from the contact of the dissimilar metals. This technique has been used by Rowe¹³⁸ to study the corrosion behaviour of coated and uncoated couples.

Guidance on conducting and evaluating galvanic corrosion tests in electrolytes is given in ASTM G71: 1981 (R1986).

Soil Tests

Soil corrosion does not lend itself readily to direct study in the laboratory. However, indirect methods involving the action of differential aeration cells have yielded valuable information in comparing the probable corrosivities of different soils towards steel. The details of this technique were described by Denison¹³⁹, Ewing¹⁴⁰, Schwerdtfeger¹⁴¹⁻¹⁴⁴, and by Logan, Ewing and Denison¹⁴⁵.

The Schwerdtfeger¹⁴¹⁻¹⁴⁴ 'polarisation break' and the polarisation resistance methods have been studied by Jones and Lowe¹⁴⁶ in relation to their effectiveness in evaluating corrosion rates of buried metals. A Holler bridge circuit was used to remove *IR* contributions during the measurement of the polarised potential. Jones and Lowe, on the basis of their studies of buried steel and aluminium specimens, concluded that the polarisation resistance was the most useful, and that the polarisation break had the serious limitation that it was difficult to identify the breaks in the curve.

Accelerated Tests—Electrolytic Tests

In view of the electrochemical nature of corrosion, it has seemed reasonable to many investigators to assume that suitable accelerated corrosion tests could be made by observing the response to electrolytic stimulation of the corrosion processes, or by attaching particular significance to the results of quickly made electrode potential and current measurements.

Acceleration of corrosion by electrolytic stimulation has sometimes been found to distort normal corrosion reactions to such an extent that the results bear no consistent relationship to ordinary corrosion and are, therefore, quite inconsistent and unreliable. This was shown, for example, by a series

of tests sponsored by ASTM Committee B-3¹⁴⁷⁻¹⁴⁸. Nevertheless, considerable success has been achieved over the development of the electrochemical potentiokinetic reactivation (EPR) test as an accelerated method for the detection of sensitisation in austenitic stainless steels. This is discussed subsequently in the section concerned with intergranular attack of Cr-Ni-Fe alloys.

Some investigators^{149, 150} have advocated a type of accelerated test in which the specimens are coupled in turn to a noble metal such as platinum in the corrosive environment and the currents generated in these galvanic couples are used as a measure of the relative corrosion resistance of the metals studied. This method has the defects of other electrolytic means of stimulating anodic corrosion, and, in addition, there is a further distortion of the normal corrosion reactions and processes by reason of the differences between the cathodic polarisation characteristics of the noble metal used as an artificial cathode and those of the cathodic surfaces of the metal in question when it is corroding normally.

Measurements of open-circuit potentials relative to some reference electrode have been assumed on occasion to provide a means of rating metals as to their relative resistance to corrosion on the basis that the more negative the measured potential, the higher will be the rate of corrosion, but this assumption is obviously invalid, since it disregards polarisation of the anodic and cathodic areas.

Some examples have been given of the use of potential measurements in corrosion tests and it is of interest to outline here certain test procedures that are used industrially to supplement or replace the more tedious and prolonged laboratory and field tests. These tests frequently rely on changing the potential as a means of accelerating the test, and although, as emphasised above, this is capable of distorting the mechanism, it is less likely to do so than a change in the nature of the environment, an increase of temperature, etc. The majority of these tests are used for evaluating electrodeposits, anodised coatings and paint films.

Electrolytic Oxalic Acid Etching Test

This test has been developed and used by Streicher¹⁵¹⁻¹⁵⁴ as a screening test to be used in conjunction with the tedious boiling nitric acid test for assessing the susceptibility of stainless steels to intergranular attack as specified in ASTM A262:1986, and will be considered subsequently in the section concerned with intergranular attack of Cr-Ni-Fe alloys.

The Electrolytic Corrosion (EC) Test

The EC test was developed by Saur and Basco¹⁵⁵⁻¹⁵⁸ for decorative Cu (optional) + Ni + Cr electrodeposits. After an appropriate area is masked off and cleaned with a slurry of MgO, the specimen is immersed in test solution *A* or *B* (Table 19.2). It is held by means of a potentiostat at +0.3 V (vs. S.C.E.) and taken through cycles of 1 min anodically polarised, 2 min unpolarised.

Table 19.2 Electrolytic corrosion test: composition of test solutions (A, B) and indicators (C, D)¹⁵⁵⁻¹⁵⁸

	Concentration			
	A	B	C	D
NaNO ₃ (g l ⁻¹)	10	10		
NaCl (g l ⁻¹)	1.3	1.0		
HNO ₃ (conc.; g l ⁻¹)	5	5		
1,10-Phenanthroline hydrochloride (g l ⁻¹)		1.0		
KCNS			3	3
Acetic acid (glacial, ml l ⁻¹)			2	2
Quinoline (ml l ⁻¹)			8	
H ₂ O ₂ (30%) (ml l ⁻¹)				3

The extent of pitting is estimated by a special microscopical technique, or by the attack on the substrate using an appropriate indicator. Thus in the case of steel 1,10-phenanthroline hydrochloride is added to the electrolyte (solution B) to detect the formation of Fe²⁺ ions. Alternatively, the specimens can be removed from the corrosion test solution and placed in an indicator solution, i.e. solution C for zinc-base die castings and solution D for steels.

The test is much faster than the CASS test (see page 19:49) and is probably more reproducible; more important is the fact that it has been correlated with service exposure.

Impedance (Aztac) Test

The impedance test¹⁵⁹ for anodised aluminium (ASTM B457:1967 (1980)) employs a 1 V r.m.s. 1 kHz source applied to a test cell in an impedance bridge; the electrolyte solution is 3.5% NaCl. The results are expressed as kilo-ohms, and whereas a bare Al specimen will give a value of about 1 kΩ, a well-scaled anodised coating will give a value of 100 kΩ. The admittance test (BS 1615:1987 and BS 3987:1974) is essentially the same as the impedance test but uses 3.5% K₂SO₄ rather than 3.5% NaCl. An admittance of < 500/*t* μS (where *t* is the thickness of the film in μm) denotes good sealing. It should be noted that thickness of the sealed coating should be specified in both tests.

Accelerated Tests — Simulated Environments

Spray Tests

The most common of the spray tests is the salt-spray or salt-fog test which was developed originally by Capp¹⁶⁰ in 1914 for studying the protective values of metallic coatings on steel under conditions that he hoped would simulate exposure to a sea-coast atmosphere. Since then the test has been used for a number of purposes, for many of which it is not well suited¹⁶¹⁻¹⁶³.

Although there is no standard size or shape of salt-spray box certain other features of the test have been standardised in ASTM B117:1990. Various

factors affect the rate of attack and Fig. 19.11 shows the effect of angle of exposure of the specimen to the salt droplets, which fall vertically from the spray nozzle, based on early work by May and Alexander¹⁶⁴. It can be seen that maximum corrosion occurs at angles between about 30 and 80° to the horizontal; vertical exposures were found to give erratic results.

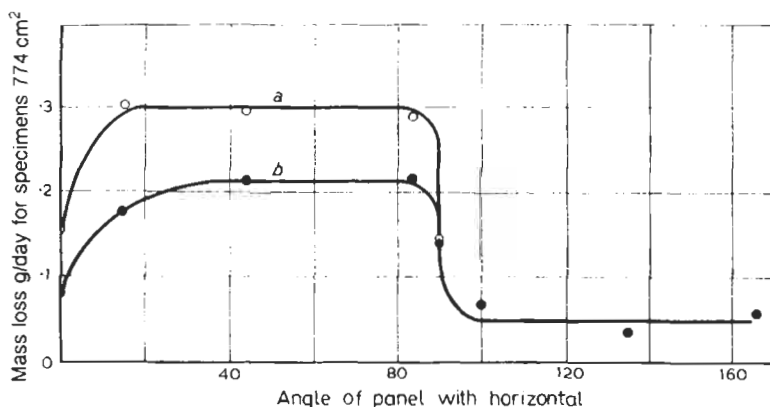


Fig. 19.11 Effect of specimen position on corrosion in salt-spray tests; specimens of cold-rolled steel. (a) 20% NaCl, (b) synthetic sea-water

There may be variations from box to box, depending on differences in fog characteristics as influenced by the design of the spray nozzles, the pressure at which the brine enters the nozzle, and the constancy of this pressure¹⁶⁵.

The results will also be influenced by the concentration of NaCl solution sprayed—some metals are affected more by one concentration than another—for example, zinc is corroded most by a concentrated brine (20%), while iron is corroded most by a dilute brine (3%); synthetic sea-water is less corrosive to these metals than either brine. In view of the many other ways by which the conditions within a salt-spray box differ from those of exposure to a natural sea-coast environment, there seems to be no great advantage in making-up complicated synthetic sea-waters for use in salt-spray testing. However, tablets for this purpose are commercially available.

Some modified brines have been used in salt-spray boxes for particular purposes, such as the acetic acid-modified brine developed by Nixon¹⁶⁶ to reproduce the type of blistering frequently encountered on chromium-plated zinc-base die castings. An acetic acid-salt-spray test has been adopted by ASTM (ASTM G85:1985 (1990)) and other modifications of the spray test covered by the same standard practice include the cyclic acidified salt spray test, the acidified synthetic sea-water spray test and the SO₂ salt spray test. Corresponding tests in the BS series are covered by BS 1224:1970. In addition the original acetic acid-salt-spray test has been modified by including cupric chloride in the brine. This is called the CASS (Copper Accelerated Acetic Acid Salt-Spray) Test; ASTM B368:1985 test. It is used extensively for testing nickel-chromium coatings on steel and zinc. The original acetic acid-salt-spray test, is modified in an important aspect by the addition of

0.25 g l⁻¹ of CuCl₂ · 2H₂O, to the 5% NaCl test solution, which substantially increases the corrosivity of the solution, especially to nickel. The addition of FeCl₃ to the acetic acid-salt-spray solution, such as is used in the Corrodokote test, was early noted to be troublesome in that it tended to precipitate. For this reason, ferric iron is not included in the CASS test solution. Essential details^{167,168} include control of cabinet temperature at 49°C, control of saturation temperature at 57°C, control of collection rate at 1.5 ± 0.5 m h⁻¹ per 80 cm² of specimen surface, control of pH by addition of acetic acid to 3.2 ± 0.1 , and an operating air pressure of 103.4 ± 6.9 kN m⁻². Higher pressure may be required to achieve the specified collection rate in 'walk in' cabinets.

It has been shown that chromium is virtually unattacked by the CASS test solution¹⁶⁹. Nickel, on the other hand, is corroded at a substantial rate (about 0.072 mm/y), the presence of the copper ions tending to maintain the nickel in an active state^{169,170}. Thus, in the CASS test (and in the Corrodokote test as well) accelerated galvanic corrosion of the nickel occurs at any discontinuities in the chromium layer. Good correlation between the results of the CASS test and the performance of plated parts in service has been reported¹⁶⁹.

Corrodokote Test^{167,171}

This is a refinement of an earlier test in which melted street slush together with its contained dirt, salts, etc. was splashed upon plated parts by means of a rotating paddle wheel. Parts soiled in this manner were then exposed to a warm, humid atmosphere. The results were striking and significant in that they closely paralleled service experience. The 'paddle-wheel test' was intended to simulate the conditions to which plated parts on automobiles are subjected when cars are garaged, unwashed, after being driven over salted slush-covered city streets on typical winter days. Platings of inadequate thickness and quality have frequently been observed to show signs of failure after only a few weeks' or even a few days' use under such circumstances. Despite certain limitations, good correlation has been reported between the results of the Corrodokote test and service performance of plated components¹³⁶, and it is now included in ASTM B380:1985 and BS 1224:1970 and ISO 4541:1978. Reagents for use in this test are prepared as follows.

1. The cupric nitrate reagent contains 2.5 g CuNO₃ · 3H₂O, dissolved in 500 ml distilled water.
2. The ferric chloride reagent contains 2.5 g FeCl₃ · 6H₂O, dissolved in 500 ml distilled water. This reagent should not be kept longer than two weeks.
3. The ammonium chloride reagent contains 50 g NH₄Cl, dissolved in 500 ml distilled water.
4. The Corrodokote slurry is prepared by mixing 7 ml of the cupric nitrate reagent, 33 ml of the ferric chloride reagent, and 10 ml of the ammonium chloride reagent with 30 g of kaolin to form a homogeneous slurry, which is sufficient slurry to cover about 2.79 m² of plated surface. A fresh batch of slurry should be made up each day.

5. The surfaces to be tested should be coated with the slurry by brushing with a circular motion, finishing with brush strokes in one direction. The coating should then be allowed to dry for 1 h, after which the coated specimen should be put into a non-condensing humidity cabinet at 38°C and from 90 to 95% r.h. After 20 h in the cabinet the specimen should be removed for inspection. Zinc die castings should be cleaned with running water and dried before inspection. Steel specimens should be examined before cleaning and the number of rust spots counted. Since most of the rust will come off with the Corrodokote coating, it may be difficult to distinguish after cleaning between surface pits and pin holes reaching the basis metal. Steel parts may be returned to a condensing humidity cabinet for 24 h or to a salt-spray cabinet for 4 h. Either supplementary exposure will bring out rust spots again.

One cycle of the Corrodokote test will reliably reveal coatings that will not endure one winter's normal use in a typical city which uses salt to de-ice its streets. In contrast, several cycles of the Corrodokote test are generally required to 'fail' coatings which will withstand one or more such winter's use.

In this connection, there is some indication that while the Corrodokote test can be depended upon to reveal coatings of unsatisfactory durability, there has been some question as to its ability to distinguish between, or to predict the relative protective value or length of useful life of, different coating systems in the very good or excellent durability range.

Also of questionable significance is the practice of shortening the Corrodokote cycle, to say 4 h, for the purpose of evaluating the durability of relatively thin coatings intended for use under comparatively mild conditions such as indoors or the interiors of automobiles, since by far the greatest amount of corrosion (of the nickel) appears to occur during the early part of the Corrodokote humidity cycle. Good correlation between the Corrodokote test and service performance has been obtained by Bigge¹⁷¹.

Sulphur Dioxide Tests

Historically, two tests in which sulphur dioxide is the principal corroding agent have been used i.e. the BNFMR* sulphur dioxide test^{172, 173} and the Kesternich test¹⁷⁴. These tests were investigated by the American Electroplaters Society Research Project 15 Committee early in its search for an acceptable accelerated corrosion test. They were soon abandoned, however, largely because the types of corrosion failures developed did not resemble those which occurred in actual service. Furthermore, the extreme corrosivity of the test environment to nickel (some 8.38 mm/y) appeared to place an undue premium on the integrity of the overlying chromium deposit which is virtually unattacked in the test. Thus, coatings which were substandard in respect of nickel or copper-nickel thicknesses might easily pass the test provided the chromium top-coat was completely continuous and remained so for the duration of the test. Conversely, coatings of proven merit on the basis of service experience, such as 0.039 mm of semi-bright plus bright

* British Non-Ferrous Metals Research Association.

nickel (duplex) with 0.00025 mm of conventional chromium, could be expected to fail in these SO₂ tests relatively quickly at any discontinuities in the chromium. In this connection, it is well to keep in mind that, even though the chromium may be non-porous initially, it can hardly be expected to remain so in service on an automobile, for example where it is subject to impact from sand, gravel, etc.

The BNFMR test was used in Europe for testing Ni + Cr coatings, but since 1970 it has been omitted from revisions of BS 1224. The test was also used to ensure the quality of anodic coatings on aluminium, but in the current British Standard (BS 1615:1987) the acetic acid salt spray test (BS 5466:Part 2:1977) or the copper-accelerated salt spray test (BS 5466:Part 3:1977) are specified for corrosion testing. In the UK, the Kesternich test (BS 5466:Part 8:1986), which has obtained the status of an ISO Standard (ISO 6988:1985), is only specified for checking the extent of porosity in tin (BS 1872:1984), tin/lead (BS 6137:1982) and tin/nickel (BS 3597:1984) coatings. In the USA, another version with a much more aggressive atmosphere is used to detect porosity in gold coatings on copper, nickel or silver (ASTM B735:1984) but the equivalent British Standard (BS 4292:Part 1:1989) specifies electrographic tests for this purpose.

Sulphur dioxide is not included as a corrosion test medium in the current ISO Standard for electrodeposited coatings of nickel + chromium and of copper + chromium (ISO 1456:1988). However, one important use of sulphur dioxide atmospheres as a controlled accelerated test has been for electrical (and, particularly, electronic) contacting surfaces. In this case, the concentration of SO₂ is much less than for the Kesternich test and the time of testing is much longer. There has been much international controversy on how to generate and control the low concentrations of gases used to simulate 'real' industrial atmospheres in which this type of component has to function over a long period. Therefore, there are now some differences between the IEC 68-2-49:Kc specification of 1983 and BS 2011:Part 2:Kc:1977 even though they have the same title ('Sulphur dioxide test for contacts and connections').

Because moist air containing sulphur dioxide quickly produces easily visible corrosion on many metals in a form resembling that occurring in industrial environments, ASTM have issued a Standard Practice for conducting tests in moist SO₂ (G87:1984). This suggests that such tests are well suited to detect pores or other sources of weakness in protective coatings and deficiencies in corrosion resistance associated with unsuitable alloy composition or treatments. However, it is stressed that the results obtained should only be taken as a general guide to the relative corrosion resistance of these materials in moist SO₂ service.

General Considerations of Spray and SO₂ Tests

The various corrosion tests specified for testing of articles having metallic coatings, including salt spray and SO₂ tests, have been brought together in a single British Standard (BS 5466:1988) which has nine parts, each of which has an ISO equivalent. These standards should be regarded as the main

source of information on approved test methods for ascertaining the general corrosion resistance of metallic coatings.

The salt spray test has seemed to yield the most consistent results when used to establish the relative merits of different aluminium alloys in resisting attack by marine atmospheres. The best results have been secured when the spray has been interrupted for so many hours each day¹⁷⁵.

Salt spray boxes are also used for studying the deterioration and protective value of organic coatings, although this test is of doubtful value for such purposes, since it fails to include many factors, e.g. sunlight, which affect the life of such coatings. Methods of testing organic coatings are discussed in a later section. The variable responses of different metals and coatings to the conditions that can be set up in salt spray boxes, as well as to the conditions that exist in natural atmospheres, make it impossible to determine the equivalent in some natural atmosphere of say an hour in a salt spray box.

For additional information on some of the features of the salt spray test and its limitations in respect of certain of the purposes for which it may be used, reference should be made to the book *Corrosion Testing for Metal Finishing*¹⁷⁶ prepared by the Institute of Metal Finishing.

There have been several attempts to develop rather elaborate testing machines in which specimens may be subjected to various sprays of fogs with cycles of condensation, heating and drying. The object has been to reproduce the conditions encountered by metals exposed in polluted industrial atmospheres. Such devices have been experimented with in the UK¹⁷⁷ and the USA¹⁷⁸. While it is sometimes possible by such tests to rate steels in a rough order of resistance to atmospheric corrosion, it should be appreciated that the nature of rust formed may differ from that obtained during actual exposure. It is only in rare cases that the resistance to attack by the sprays is analogous to their resistance in the natural atmosphere which the tests seek to simulate. Such parallelism is not common enough to make these tests very reliable¹⁷⁹.

Dennis and Such¹⁸⁰ point out that the BNFMRASO₂ test was really a means of detecting discontinuities in the chromium layer of a Cr + Ni coating system, and it therefore gave unfavourable results when used for testing micro-cracked or micro-porous Cr, since the Cr was rapidly undermined, with consequent flaking. Conversely, the test exaggerates the beneficial effect of crack-free Cr. The test also fails to indicate the improved corrosion resistance of duplex Ni as compared with bright Ni. A critical account of laboratory corrosion testing methods for Ni-Cr coatings is given by Dennis and Such¹⁸¹.

Accelerated Tests for Weathering Steels

Recent interest in weathering steels has stimulated work on accelerated laboratory tests which can be used to investigate the effect of alloy composition on performance. It is well established that a wetting and drying cycle should be an integral part of any laboratory test in which the characteristic properties of weathering steels are revealed¹⁸², and Bromley, Kilcullen and

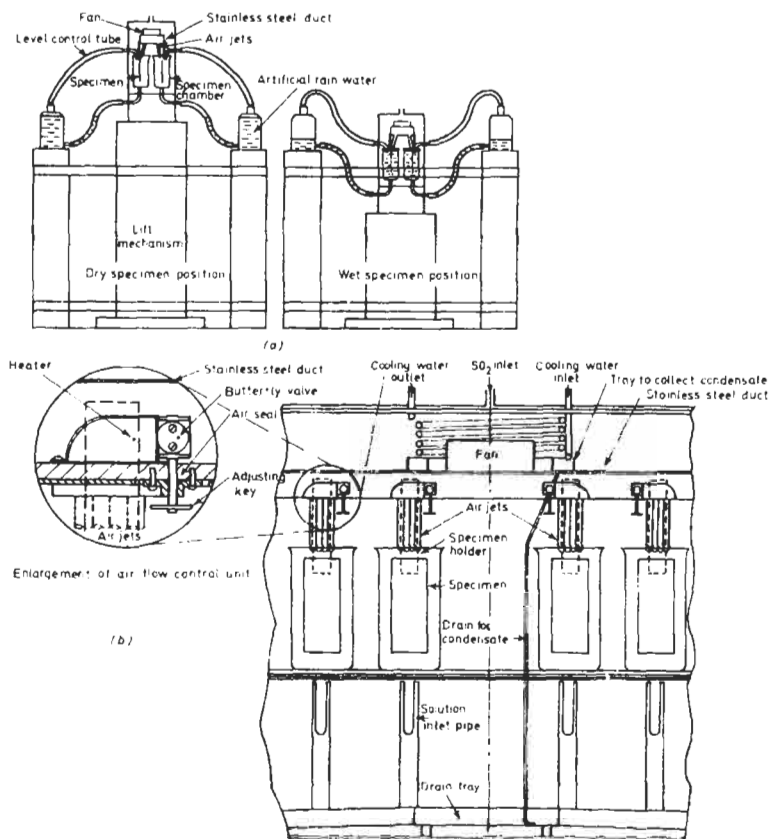


Fig. 19.12 Rig used for a laboratory evaluation of weathering steels. (a) General layout of rig showing unimmersed and immersed position and (b) detailed view of central portion of cabinet (after Bromley, Kilcullen and Stanners¹⁸³)

Stanners¹⁸³ have designed a test rig (Fig. 19.12) which provides results that can be correlated with actual atmospheric exposure data. The rig has been designed to investigate a wide range of alloying elements in a development programme on slow-weathering steels for which it was essential to have a rapid, reliable and reproducible test that incorporated the specific atmospheric factors responsible for rust formation.

The results obtained with this equipment show that the corrosion rate in the rig is about four times that encountered in an industrial UK atmosphere. This acceleration, however, is not achieved by accentuating any of the environmental factors, but rather by holding them near to the worst natural conditions for as long as possible. The procedure used ensures that the rust film is completely dried for short periods, thus simulating the conditions that bring out the beneficial effects of protective rust films on the steels under study.

The use of electrochemical tests for rapid assessment of the performance of these steels has attracted interest, and Pourbaix¹⁸⁴ has devised an appa-

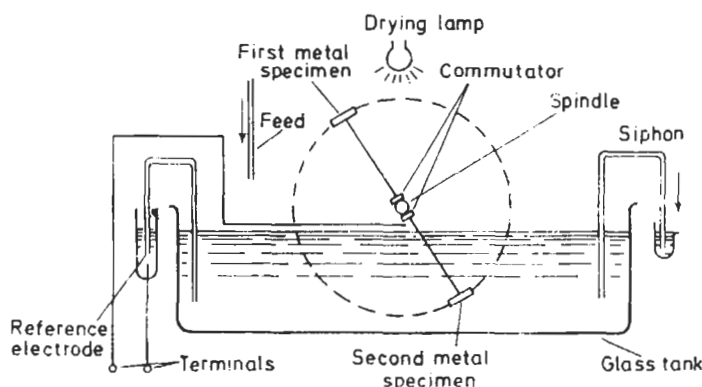


Fig. 19.13 Equipment for studying 'patina' formation on low-alloy steels (after Pourbaix¹⁸⁴)

ratus in which potential measurements are used to evaluate the protective nature of corrosion products formed on low-alloy steels, such as the weathering steels, during periodic wetting and drying. The apparatus (Fig. 19.13) consists of a glass tank containing an appropriate electrolyte, such as a natural or artificial water. Two specimens of the metal or alloy under study are attached to a spindle which rotates slowly (about 1 rev/h) so that the specimen is immersed in the solution for approximately half the time and exposed to the atmosphere for the remainder. An electric lamp is placed above the tank so that the specimens remain wet for a time after withdrawal from the solution, but are completely dried during the cycle. Measurement of the potentials of the specimens at the beginning and end of the immersion period is effected by means of the commutators, which are attached to the spindle but electrically insulated from it, and a reference electrode. The e.m.f. taken from the terminals can be fed to a multipoint recorder so that a recording of the E -time relationship may be obtained for each specimen. The solution can be made to circulate slowly by allowing it to drip in from a feed and overflow via a siphon. In a variation of the apparatus a Luggin capillary is attached to the sample so that the potentials can be measured during the period when the specimen has emerged from the solution but is still wet.

Figure 19.14 shows results obtained from the apparatus for different steels some of which (Nos. 1, 2, 3 and 7) form a protective patina of corrosion products, whilst others (Nos. 4, 5, and 6) form patinas that are non-protective; the criterion adopted is that the more positive the potential the more protective is the rust patina¹⁸⁴.

Legault, Mori and Leckie^{185, 186} have used open-circuit potential vs. time measurements and cathodic reduction of rust patinas for the rapid laboratory evaluation of the performance of low-alloy weathering steels. The steel specimens are first exposed for 48 h to the vapour of an $0.001 \text{ mol dm}^{-3}$ sodium bisulphite solution maintained at 54°C (humid SO_2 -containing atmosphere) to stimulate corrosion under atmospheric conditions. They are then subjected to two types of test: (a) open-circuit potential-time tests for periods up to 3 000 s in either distilled water or $0.1 \text{ mol dm}^{-3} \text{Na}_2\text{SO}_4$ and

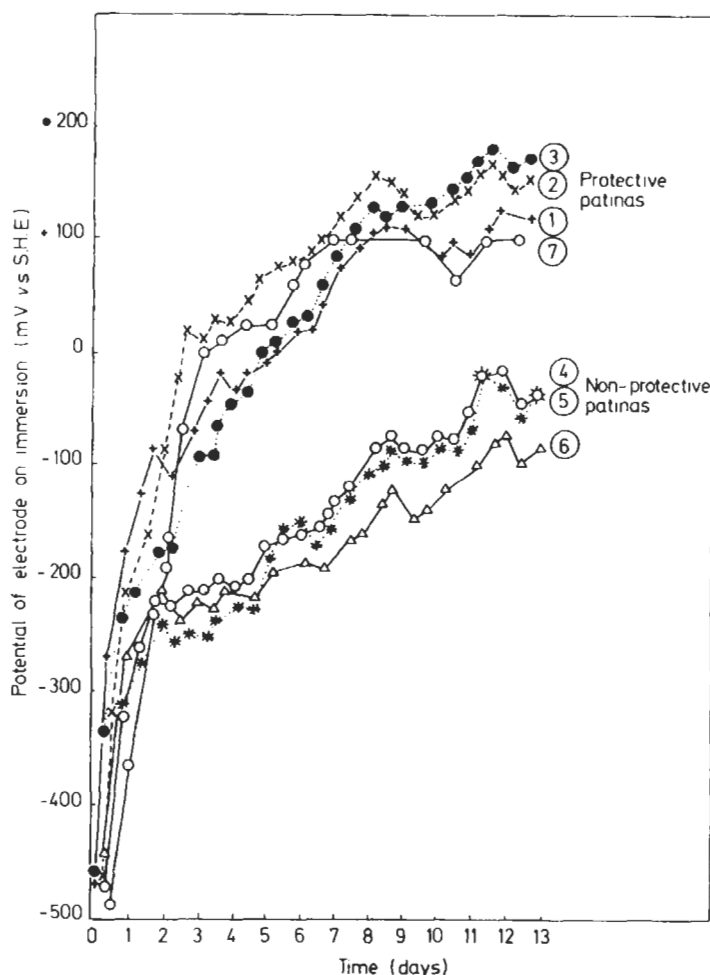


Fig. 19.14 Relationship between E (vs. S.H.E.) and time for steels that form a protective patina (Nos. 1, 2, 3 and 7) and those that form a non-protective patina (Nos. 4, 5 and 6). E is determined by the equipment shown in Fig. 19.13 and is determined during initial immersion of the specimen (after Pourbaix¹⁸⁴)

(b) cathodic reduction in $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ at $1 \text{ mA cm}^{-2} \text{ c.d.}$ In the cathodic reduction experiments, which provide a means of evaluating the degree of rusting¹⁸⁷, both the potential and time are recorded, the onset of hydrogen evolution at constant potential being taken as the end point and giving the *oxide-reduction time*.

In order to evaluate the tests determinations were carried out on the steels that had been exposed to the atmosphere for 1, 2, 3, 4 and 6-month periods. It was established that the initial open-circuit potential and the decrease in potential (more negative) with time varied with the nature of the steel and the time of exposure to the atmosphere, and the maximum negative potential was taken as a measure of corrosion resistance; the more negative the

potential the lower the resistance of the alloy. In the case of three alloy steels that differed only in copper content it was found that the open-circuit potential was related to the corrosion rate as assessed by conventional weight loss.

A relationship was also established between the oxide-reduction time and time of exposure, and the results for a mild steel and a 1Cu-3Ni weathering steel were similar to those obtained by mass loss. The authors give various expressions that relate oxide-reduction time (min) with corrosion rate (mm/y), and claim that a short exposure to a laboratory SO₂ atmosphere followed by determining the *E* vs. time and oxide-reduction time provides a rapid method of evaluating weathering steels.

Intergranular Attack of Cr-Ni-Fe Alloys

Early in the history of stainless steels it was recognised that they were highly susceptible to intergranular attack resulting from the precipitation of Cr-Fe carbides with the consequent depletion in the chromium content at grain boundaries when the alloy was heated in a specific range of temperature (see Sections 1.3, 3.3 and 9.5). It was necessary, therefore, to develop methods of testing that would detect susceptibility to intergranular attack as influenced by variations in processing and/or composition. As will be seen, most reagents used for these tests are highly aggressive, and it is important to note that an alloy found to be susceptible during testing will not necessarily be attacked intergranularly under the milder environmental conditions that may prevail in service.

Brown¹⁸⁸ has pointed out that Du Pont use evaluation tests for (a) as-received unstabilised alloys containing more than 0.03% C to check the effectiveness of the final heat treatment and (b) stabilised or special low-carbon grades after a sensitising treatment (1 h at 677°C) to determine whether susceptibility might develop during a subsequent welding operation.

Intergranular corrosion of Fe-Ni-Cr alloys has been the subject of a comprehensive review by Cowan and Tedmon¹⁸⁹ who summarised the various tests used for determining susceptibility (Table 19.3). Of these tests, Nos. 1-5, which are regarded as reliable test procedures by the ASTM, have been incorporated into ASTM A262:1986 'Recommended Practice for Detecting Susceptibility to Intergranular Attack in Stainless Steel' as follows:

Practice A—10% oxalic acid, electrolytic etching at ambient temperatures

Practice B—Boiling 50% H₂SO₄ + 25 g l⁻¹ Fe₂(SO₄)₃

Practice C—Boiling HNO₃

Practice D—10% HNO₃ + 3% HF at 70°C

Practice E—Boiling 16 wt. % H₂SO₄ + 5.7% CuSO₄ + metallic copper

It should be noted that although ASTM A262:1986 provides details of test procedures no information is given on typical corrosion rates or acceptable limits for various heat-treated alloys, which are regarded as outside the province of a specification that describes test procedures. Table 19.4, taken from a paper by Brown¹⁸⁸, shows the maximum acceptable evaluation test rates specified by the Du Pont Company for various alloys tested by the acid

Table 19.3 Summary of chemical tests used for the determination of susceptibility to intergranular corrosion of iron-nickel-chromium alloys*

Test name	Ref.	Usual solution composition	Test procedure	Quantitative measure	Potential range (V vs. S.H.E.)	Species selectively attacked
1. Nitric acid test	†	65 wt.% HNO ₃	Five 48 h exposures to boiling solution; refreshed after period	Average mass loss per unit area of five testing periods	+ 0.99 to + 1.20	1. Chromium-depleted areas 2. σ -phase 3. Chromium carbide
2. Acid ferric sulphate (Streicher) test	†‡	50 wt.% H ₂ SO ₄ + 25 g/l ferric sulphate	120 h exposure to boiling solution	Mass loss per unit area	+ 0.7 to + 0.9	1. Chromium-depleted areas 2. σ -phase in some alloys
3. Acid copper sulphate test	†§	16 wt.% H ₂ SO ₄ + 100 g/l CuSO ₄ (+ metallic copper)	72 h exposure to boiling solution	1. Appearance of sample upon bending 2. Electrical resistivity change 3. Change in tensile properties	+ 0.30 to + 0.58	Chromium-depleted area
4. Oxalic acid etch	†	100 g H ₂ C ₂ O ₄ · 2H ₂ O + 900 ml H ₂ O	Anodically etched at 1 A/cm ² for 1.5 min	1. Geometry of attack on polished surface at $\times 250$ or $\times 500$	+ 1.70 to + 2.00 or greater	Various carbides
5. Nitric-hydrofluoric acid test	¶	10% HNO ₃ + 3% HF	4 h exposure to 70°C solution	Comparison of ratio of mass loss of laboratory annealed and as-received samples of same material	Corrosion potential of 304 steel = +0.14 to +0.54	1. Chromium-depleted areas 2. Not for σ -phase 3. Used only for Mo-bearing steels
6. Hydrochloric acid test	¶	10% HCl	24 h in boiling solution	1. Appearance of sample after bending around mandril 2. Mass loss per unit area	(a) Redox potential = +0.32 (b) Corrosion potential = -0.2 \pm 0.1	1. Alloy-depleted area 2. Not for σ -phase
7. Nitric acid Cr ⁶⁺ test		5 N H ₂ SO ₄ + 0.5 N KCr ₂ O ₇	Boiling with solution renewed every 2-4 h for up to 100 h	1. Mass loss per unit area 2. Electrical resistivity 3. Metallographic examination	(a) Redox potential = +1.37 (b) Corrosion potential of 304 steel = +1.21	Solute segregation to grain boundaries

* Data after Cowan and Tedmon¹⁹⁹

† ASTM A262:1986 and Practice G28-1985

‡ M. A. Streicher, ASTM Bulletin No. 229, 77-86 (1958) G28-1985.

§ ASTM A 262:1986

¶ D. Warren, ASTM Bulletin No. 230, 45-56 (1958).

|| J. S. Armijo, *Corrosion*, 24 (1968).

Table 19.4 Maximum acceptable evaluation test rates specified by Du Pont for services where susceptible material would be intergranularly attacked*

Type	Condition	Max. corrosion rate mm/y
120 h acid $\text{Fe}_2(\text{SO}_4)_3$ test (ASTM A-262, Practice B)		
304	As received	1.22
304L	20 min at 677°C	1.22
316	As received	1.22
316L	20 min at 677°C	1.22
317L	20 min at 677°C	1.22
CF-8	As received	1.22
CF-8M	As received	1.22
240 h HNO_3 test (ASTM A-262, Practice C)		
304	As received	0.457
304L	20 min at 677°C	0.305
304L	1 h at 677°C	0.610
309S	As received	0.305
316	As received	0.457
347	1 h at 677°C	0.610
CF-8	As received	0.610
CF-8M	As received	0.762

* Data after Brown¹⁸⁸.

ferric sulphate test and by the Huey test. It should be noted that evaluation tests are specified by Du Pont when it is known or suspected that the environmental conditions in service are conducive to intergranular attack of susceptible material.

The reagents used in Practice B to E all have a high redox potential and Cowan and Tedmon¹⁸⁹ have presented schematic E -log i curves (Fig. 19.15) showing the range of potentials of the various tests and the relative rates of attack on the matrix (Fe-18Cr-10Ni) and the chromium-depleted alloy at the grains boundaries, which has been assumed for this purpose to have a composition Fe-10Cr-10Ni, in a hot reducing acid. Although this diagram cannot show the effect of alloy composition, nature of test solution, conditions of test, etc. on intergranular attack, it serves to illustrate the electrochemical principles involved in the test procedures, all of which are based on reagents that attack the intergranular sensitised areas at a higher rate than the matrix; this may lead to the dislodgement of whole grains with a consequent high mass loss.

Boiling HNO_3 Test

This test, which is frequently referred to as the Huey test, was first described and used by W. R. Huey¹⁹⁰ in 1930, and since that time it has had wide application, particularly in the USA. The test consists of exposing the specimens (20–30 cm²) in fresh boiling 65% HNO_3 (constant boiling mixture) for five successive periods of 48 h each under a reflux condenser. The specimens are cleaned and weighed after each period, and the corrosion rate (as a rate of penetration) is calculated for each period of test and for the average over the five periods; corrosion rates are expressed as mm/y. The reason for the

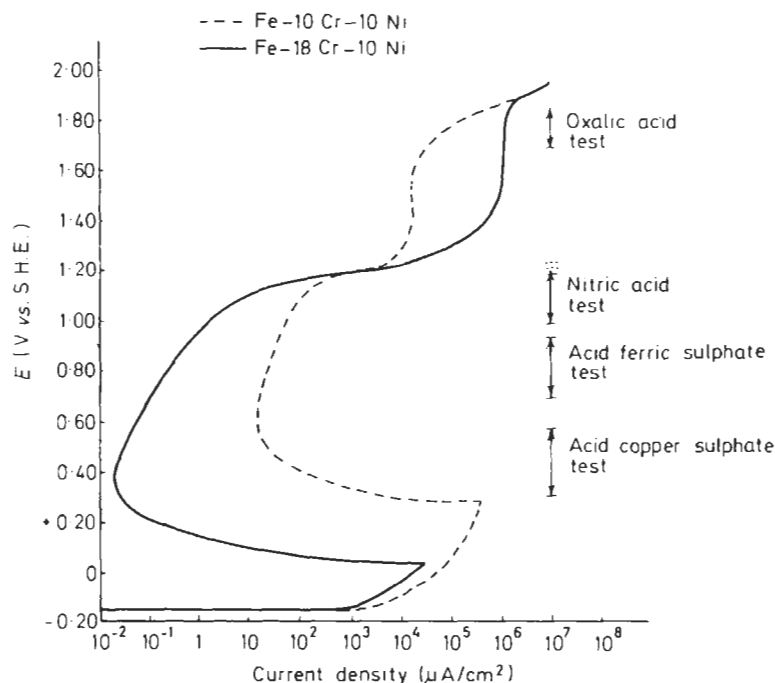


Fig. 19.15 Schematic representation of range of corrosion potentials expected from various chemical tests for sensitisation in relation to the anodic dissolution kinetics of the matrix (Fe-18Cr-10Ni stainless steel) and grain boundary alloy (assumed to be Fe-10Cr-10Ni) owing to depletion of Cr by precipitation of Cr carbides of a sensitised steel in a hot reducing acid (after Cowan and Tedmon¹⁸⁹)

above procedure is due to the fact that Cr(VI) ions, produced from the oxidation of Cr²⁺ and Cr³⁺ by the HNO₃, if allowed to accumulate in the HNO₃, markedly increase its aggressiveness so that severe intergranular attack with grain dislodgement can occur even with solution-annealed steel free from precipitated carbides; hence the necessity for the periodic changing of the solution and for a minimum ratio of solution volume to area of specimen (at least 20 ml HNO₃/cm² of stainless steel). Brown¹⁸⁸ points out that during a normal test the Cr(VI) content will not reach a level where an acceleration in rate occurs unless the specimen is in the sensitised condition, and under these circumstances the presence of Cr(VI) is an advantage in discriminating between sensitised and unsensitised material.

Maximum corrosion rates used by Du Pont for various alloys are given in Table 19.4, and most users of the test consider average corrosion rates of 0.46–0.61 mm/y and 0.76 mm/y to represent the upper limits for satisfactory resistance for wrought austenitic alloys and cast austenitic alloys, respectively. Streicher¹⁵³ considers that if the corrosion rate for each period increases over that for the previous period the alloy is susceptible.

The mechanism of the corrosion reaction is not clear, particularly in view of the changes in composition of the HNO₃ that take place during the 48 h period of the test. Streicher¹⁵³ reports that the corrosion potential of the

steel ranges from 1.00 to 1.20 V (vs. S.H.E.) during the test owing to the accumulation of Cr(VI), and it can be seen from Fig. 19.15 that the sensitised areas will have a higher corrosion rate than the matrix throughout this potential range, although they will become similar at the higher potentials. The high corrosion rates obtained in the test are due partly to intergranular attack and partly to the undermining and dislodgement of grains.

Stainless steels and Ni-base alloys containing Mo, such as type 316L (0.03% C max.) and Hastelloy C, are found to give very high corrosion rates in the HNO₃ test even when they are immune to intergranular attack when subjected to other tests that reveal sensitisation due to chromium-depleted zones; furthermore, such alloys even after being subjected to a sensitising heat-treatment do not give rise to intergranular attack in most conditions of service. This high corrosion rate is considered to be due to the formation of a submicroscopic σ -phase, and although positive proof is not available its presence is substantiated by the fact that the phase becomes identifiable after longer periods at the sensitising temperatures, although in this form it has little effect on the corrosion rate. It would appear that the σ -phase dissolves rapidly during the HNO₃ test, and since it has a high chromium content the solution becomes enriched in Cr(VI) with a consequent increase in the corrosion rate of the alloy. It follows that the test is unsuitable for evaluating the behaviour of stainless steels that may precipitate σ -phase, unless the alloy is to be used in service for nitric acid plant.

Henthorne¹⁹¹, in considering the corrosion testing of weldments, points out that the test will also give high rates due to (a) end-grain attack, which is particularly prevalent in resulphurised or heavily cold-worked material and (b) dissolution of Ti(C, N) such as occurs in Type 321 weldments and leads to knife-line attack. Since most service conditions do not cause attack on the alloy in these conditions the test can be misleading.

Thus, under the circumstances already outlined, the test can be misleadingly severe, but it is particularly valuable for evaluating alloys for use in HNO₃ or in other strongly oxidising acid solutions to ensure that they have received the correct heat treatment and have an appropriate composition, i.e. a low carbon content or the correct ratio of (Ti or Nb)/C.

Boiling H₂SO₄ + CuSO₄ Tests

The use of boiling H₂SO₄ + CuSO₄ for detecting intergranular sensitivity was first described by Strauss, *et al.*¹⁹² in 1930, and is frequently referred to as the Strauss test, although the conditions of the test have been modified; whereas the Huey test is most widely used in the USA the Strauss test has been the preferred test in Europe. The test is mild compared to the Huey test and intergranular attack takes place with little grain dislodgement.

The use of metallic copper chips placed in contact with the steel to speed up the test and thus decrease the time of testing was first described by Rocha¹⁹³, and subsequent work by Streicher¹⁵⁷ showed that its presence significantly increased the rate of intergranular attack even when it was not in contact with the steel. Approximate mass losses for a sensitised Type 316 stainless steel during a 240 h testing in boiling H₂SO₄ + CuSO₄ are as follows:

No metallic Cu present	0.1 g dm^{-2}
Metallic Cu present, but not in contact with the steel	1.0 g dm^{-2}
Metallic Cu in contact with steel	4.0 g dm^{-2}

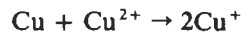
As used in Germany the composition of the solution is 110 g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 100 ml H_2SO_4 (s.g. 1.84) and 1 l of water, the test being conducted for 168 h in the boiling solution. The ASTM Tentative Procedure A393-63T specified a similar composition containing 100 g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 100 ml H_2SO_4 (s.g. 1.84) with water added to make a total volume of 1 l. The test time was 72 h, and with the high carbon contents of the earlier steels this was adequate for detecting susceptibility. However, with the decrease in the carbon contents of stainless steels a more prolonged boiling time was found to be necessary, and Scharfstein and Eisenbrown¹⁹⁴ showed that a Type 304 stainless steel containing 0.068% C would pass the 72 h Struss test even after a sensitising treatment of up to 4 h at 677°C. For this reason A393-63T has been discontinued and in ASTM A262:1986 Practice E, the specimens are placed in contact with metallic copper chips to increase the rate of intergranular attack^{153,188}. This test is of comparable sensitivity to the other tests, and is far more discriminating than the older tentative standard; furthermore, it is more severe so that the testing time is decreased from 72 to 24 h. This test has been incorporated in the international standard ISO 3651-2:1976.

Figure 19.15 shows that the corrosion potential of stainless steel in the $\text{H}_2\text{SO}_4 + \text{CuSO}_4$ test lies in the range 0.30–0.58 V, and that whereas the corrosion rate of the unsensitised alloy is approximately $10^{-1} \mu\text{A cm}^{-2}$, that of the sensitised material is $10 \mu\text{A cm}^{-2}$; for heavily sensitised material the ratio of rates¹⁸⁹ of sensitised:unsensitised alloy may be as high as $10^5:1$. This large difference in rates leads to rapid attack, which is confined to the depleted zone having a thickness of the order of $1 \mu\text{m}$, and under these circumstances there will be little grain dislodgement. Thus, the mass change will be so small that it cannot be used as a criterion of susceptibility. For this reason assessment of intergranular attack is normally carried out (ASTM 262 Practice E) by bending the specimen around a mandrel through 180° and inspecting the bend surface for cracks. Measurements of changes in electrical resistivity¹⁵¹ and in ultimate tensile strength¹⁹⁵ are used as quantitative methods of assessment, but according to Ebling and Scheil¹⁹⁶ they are not as discriminating as the qualitative bend test.

The $\text{H}_2\text{SO}_4\text{-CuSO}_4$ test, unlike the Huey test, is specific for susceptibility due to chromium depletion and is unaffected by the presence of submicroscopic σ -phase in stainless steels containing molybdenum or carbide stabilisers. It can be used, therefore, with confidence to test susceptibility in austenitic (300 series) and ferritic (400 series) stainless steels and in duplex austeno-ferritic stainless steels such as Types 329 and 326.

The mechanism of the action of metallic copper was investigated by Streicher¹⁵³ who determined the potential of a Type 314 stainless steel, the redox potential of the solution (as indicated by a platinised-Pt electrode) and the potential of the copper. The actual measurements were made with a saturated calomel electrode, but the results reported below are with reference to S.H.E. In the absence of copper the corrosion potential of the stainless steel was 0.58 V, whereas the potential of the Pt electrode was

approximately 0.77 V. When metallic copper was introduced into the solution (not in contact with the steel) both the corrosion potential of the steel and that of the Pt electrode attained the same more negative potential of 0.37 V, the copper attaining a steady value of 0.30 V. Finally, when the stainless steel was placed in contact with the copper it took up a more negative potential of 0.30 V, the potential of the copper being unaffected. These potentials have been interpreted by Streicher and have been expressed in E - I diagrams (Fig. 19.16) showing how the corrosion potential and the corrosion rate varies with conditions of the test. Introduction of metallic copper into the solution results in the disproportionation reaction



and the accumulation of the Cu^+ ions in the solution produces a decrease in the polarisation of the local anodes on the stainless steel, which are polarised to the redox potential of the solution (Fig. 19.16*b*). Contact of copper with the stainless steel results in a further decrease in the corrosion potential of the stainless steel to that of copper, indicating that cathodic polarisation of the steel has occurred since the steel is the cathode of the stainless steel/copper bimetallic couple. There is simultaneously a reduction in the anodic polarisation of the susceptible grain boundaries, and a consequent increase in the corrosion rate (Fig. 19.16*c*). Thus, contact of the steel with the copper results in intergranular attack of the steel at constant potential, the copper acting in the same way as a potentiostat.

The Huey test is widely used in the USA whilst the H_2SO_4 - CuSO_4 test is preferred in the UK, with an increasing tendency to use the metallic copper variant. The H_2SO_4 - CuSO_4 -Cu test procedure is given in BS 5903:1980 (1987).

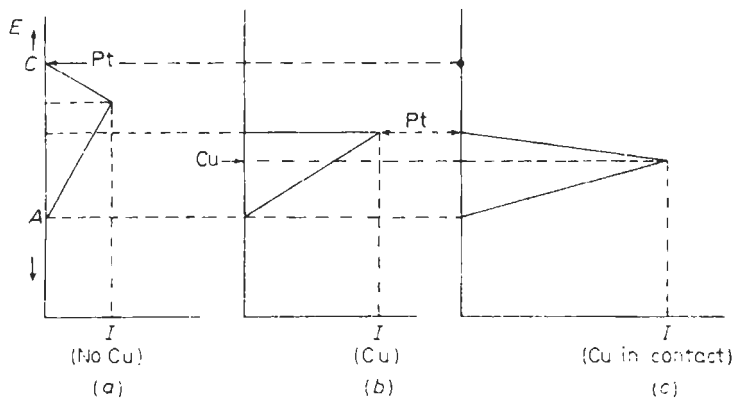


Fig. 19.16 Schematic E - I diagrams of local cell action on stainless steel in $\text{CuSO}_4 + \text{H}_2\text{SO}_4$ solution showing the effect of metallic copper on corrosion rate. C and A are the open-circuit potentials of the local cathodic and anodic areas and I is the corrosion current. The electrode potentials of a platinised-platinum electrode and metallic copper immersed in the same solution as the stainless steel are indicated by arrows. (a) represents the corrosion of stainless steel in $\text{CuSO}_4 + \text{H}_2\text{SO}_4$, (b) the rate when copper is introduced into the acid, but is not in contact with the steel, and (c) the rate when copper is in contact with the stainless steel (after Streicher¹⁵³)

HNO₃-HF Test

This test was first described by Warren¹⁹⁷ in 1958, and consists of two 2 h periods in 10% HNO₃ + 3% HF solution at 70°C using fresh solution for each period. The test is therefore more rapid than the others, and it is specific for chromium depletion by carbide precipitation since it is unaffected by the submicroscopic σ -phase formed in molybdenum-bearing steels; as described in A262:1986 its use is confined to Types 316, 316L, 317 and 317L stainless steels¹⁸⁸. Since the corrosion rates of stainless steels in the acid are high and vary greatly from test to test, it is necessary to run two tests and to compare the corrosion rates of the specimen to be evaluated ('as received' for Types 316 and 317 and in the sensitised condition for Types 316L and 317L) and another laboratory-annealed specimen of the same alloy shown to be free from precipitated carbides by the step structure produced after electrolytic etching in oxalic acid. Intergranular attack is assessed by the rate of penetration evaluated from the mass loss, and if the mass loss of the specimen to be evaluated is greater than 1.5 times that of the standard, the former is considered to be susceptible.

The solution has a low redox potential and the corrosion potentials for austenitic stainless steels will be in the range 0.14–0.54 V, according to composition. Thus it can be seen from Fig. 19.15 that all but the highest chromium steels will be in the active region, so that the test relies on vigorous corrosion of the grain boundary zones whilst the matrix remains somewhat passive and corrodes at a slower rate¹⁸⁹. Although the test gives constant and reliable results it has not been used widely for routine evaluations for the following reasons: (a) the need to use a ratio of two test rates, (b) inconvenience of handling solution containing HF and (c) the availability of the H₂SO₄ + Fe₂(SO₄)₃ test.

H₂SO₄ + Fe₂(SO₄)₃ Test (Streicher Test)

This was described in 1959 by Streicher¹⁵³, and consists of one period of exposure to a boiling solution of 50 mass% H₂SO₄ + 25 g l⁻¹ Fe₂(SO₄)₃ for 120 h, assessment being based on mass loss (see Table 19.4). Streicher, however, usually reports a ratio of mass loss of sample to be assessed/weight loss of annealed sample (g dm⁻²), and as for the HNO₃-HF test considers that a ratio > 1.5–2.0 indicates susceptibility; for Type 304 Streicher considers a rate > 0.76 mm/y to indicate susceptibility, but Brown considers a higher figure to be acceptable (see Table 19.4)

Accumulation of corrosion products does not stimulate attack so that several specimens may be tested in the same solution, but additional Fe₂(SO₄)₃ may have to be added (or the solution changed) if there is considerable attack on severely sensitised specimens, as is indicated by a colour change of the solution from brown to dark green.

The redox potential of the solution is that of the Fe³⁺/Fe²⁺ equilibrium and lies within the range 0.80–0.85 V (vs. S.H.E.). The high weight loss of susceptible alloys is due to undermining and grain dislodgement at the sensitised zones, which occurs at about twice the rate of that in the Huey test. Another difference is that whereas in the Huey test corrosion products

[Cr(VI)] increase the rate by raising the potential of the alloy into the trans-passive region, the converse applies in the acid ($\text{Fe}_2(\text{SO}_4)_3$) test, since reduction of Fe^{3+} to Fe^{2+} during the test will result in a decrease in the redox potential and the whole sample will corrode with hydrogen evolution.

According to Cowan and Tedmon¹⁸⁹ the test can selectively attack some types of σ -phase. Those of Types 321 and 347 are readily attacked, whereas the molybdenum-bearing σ -phase of Type 316 is unattacked. The test will also show Hastelloys and Inconels to be susceptible to intergranular attack when there are either chromium- (or molybdenum-) depleted grain boundaries or grain-boundary σ -phase present. Ferritic (200 series) and austenoferritic stainless steels can also be tested for chromium-depletion sensitisation in this reagent, but whether σ -phases formed in these alloys affect the test has not been established.

In conclusion it must be emphasised again that all the tests used are accelerated tests and only provide information on susceptibility to intergranular attack under the precise test conditions prevailing. They are quality control tests that may be used to demonstrate either that heat treatment has been carried out adequately or that a steel will withstand the test for a certain sensitising heat treatment.

Electrolytic Oxalic Acid Etching Test

This test, which was developed by Streicher¹⁵³, is used as a preliminary screening test to be used in conjunction with the more tedious testing procedures such as the boiling HNO_3 test. The specimens are polished (3/0 grit paper) and then anodically polarised for 1.5 min at 1 A cm^{-2} at room temperature in a solution prepared by dissolving 100 g of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in 900 ml of distilled water. The surface is then examined at about $\times 500$ magnification and the structure is classified as 'step', 'ditch' or 'dual' (both 'step' and 'ditch'). If the surface shows a 'step' structure it is immune to intergranular attack and no further testing is necessary; if the structure is 'ditch', further testing by the Huey test or some other chemical test is necessary; if 'dual' further testing may be necessary. Thus the test, by identifying

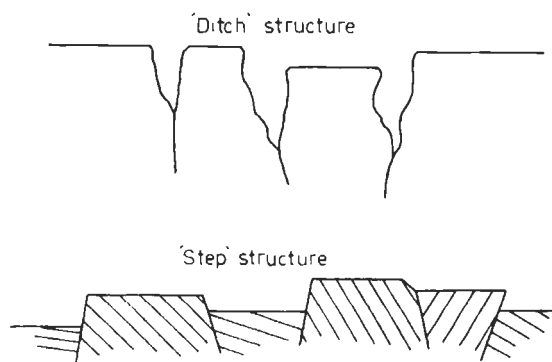


Fig. 19.17 'Ditch' and 'step' structures (after Streicher¹⁵³)

structures that are immune to intergranular attack, eliminates unnecessary testing, although where a 'ditch' (or possibly a 'dual' structure) is obtained, final confirmation by the Huey test is essential. Figure 19.17 shows diagrammatically the 'ditch' and 'step' structures, and Fig. 19.18 photomicrographs of these structures and a 'dual' structure¹⁹⁸.

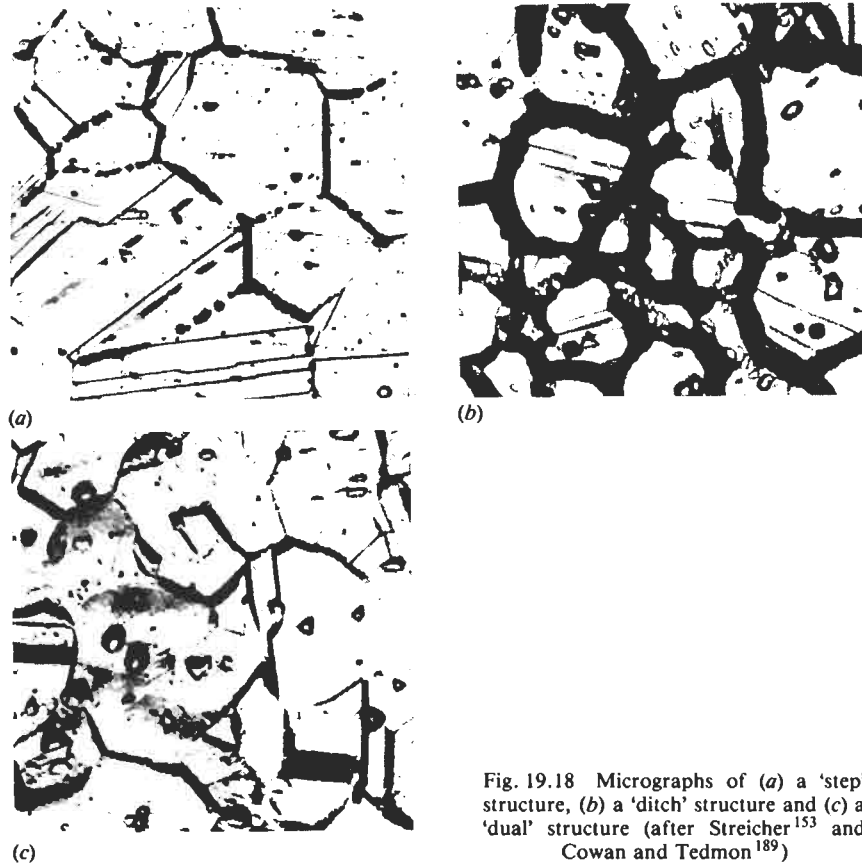


Fig. 19.18 Micrographs of (a) a 'step' structure, (b) a 'ditch' structure and (c) a 'dual' structure (after Streicher¹⁵³ and Cowan and Tedmon¹⁸⁹)

The test operates at a potential above 2.00 V (vs. S.H.E.), and the 'ditch' structure obtained with sensitised alloys must be due, therefore, to the high rate of dissolution of the sensitised areas as compared with the matrix. The 'step' structure is due to the different rates of dissolution of different crystal planes, and the 'dual' structure is obtained when chromium carbides are present at grain boundaries, but not as a continuous network.

Electrochemical Tests

The difficulties associated with the ASTM Recommended Methods for Detecting Susceptibility to Intergranular Attack in Austenitic Stainless

Steels' (A262-1986) are that the methods are destructive and qualitative in nature. Early attempts to develop quantitative, non-destructive electrochemical techniques to detect sensitisation by Clerbois *et al.*¹⁹⁹ employed potentiostatic techniques and it was observed that sensitised 18-8 stainless steel when anodically polarised potentiostatically in $1.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ gave rise to a secondary active peak in the range $0.14\text{--}0.24 \text{ V}$ (vs. S.H.E.) that was not present in the curve for the annealed alloys. This observation was criticised by France and Greene²⁰⁰, who consider that the active peak is due to the dissolution of Ni that had accumulated at the surface during active dissolution at lower potentials. Clerbois, *et al.*¹⁹⁹ also noted that if a sensitised sample is held at 0.14 V in $1.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ for 24 h and then bent around a mandrel, it fissures and cracks, and it can be seen from Fig. 19.15 that at this potential the chromium-depleted grain boundary will corrode actively, whereas the matrix will be passive. The potentiostatic test using cracking to detect susceptibility is thus analogous to the acid-copper sulphate test.

France and Greene²⁰⁰ proposed that it should be possible to predict service performance by potentiostatic studies of steels in the environments encountered in practice coupled with metallographic examination of the surfaces. They argued that many environments do not selectively attack the grain boundaries of sensitised stainless steels so that the use of costly preventative measures is unnecessary. Since the intergranular attack of austenitic stainless steels occurs only in limited potential regions it should be possible to predict service performance providing these regions are precisely characterised.

In their studies, specimens of different sensitised steels were held at various constant potentials in different concentrations of the acid under study at various temperatures and the surfaces were then examined metallographically for intergranular attack. Data obtained in this way enabled *E*-concentration of acid diagrams to be produced showing the zones of general corrosion, fine intergranular corrosion and coarse intergranular corrosion for a given sensitised stainless steel in a given acid at various constant temperatures (Fig. 19.19).

Streicher²⁰¹, however, considered this approach to be unsound and pointed out that the short duration of the potentiostatic studies carried out by France and Greene cannot be used to predict long-term behaviour in service. The prolonged dialogue between these workers^{202, 203} was well summarised in the review article by Cowan and Tedmon¹⁸⁹ who concluded that these particular potentiostatic tests cannot be regarded as *accelerated* tests for service environments and that predicting future industrial service for periods longer than the test is not advisable.

EPR Test

The electrochemical potentiokinetic reactivation (EPR) test was proposed by Cihal *et al.*²⁰⁴ and developed by Novak and others²⁰⁵⁻²⁰⁷ as a fast, quantitative and non-destructive technique for establishing the degree of sensitisation of austenitic stainless steels.

The test is accomplished by a potentiodynamic sweep from the passive

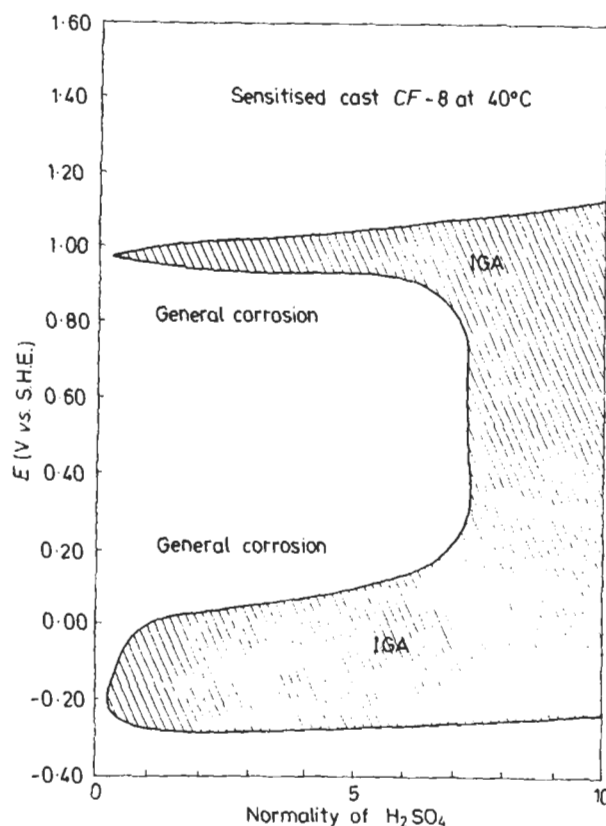


Fig. 19.19 Intergranular corrosion plot for a sensitised cast CF-8 stainless steel (0.08% C max., 8–11% Ni, 18–21% Cr) in H_2SO_4 at 40°C as a function of potential and concentration of acid (after France and Greene²⁰⁰)

to the active regions of electrochemical potential (a process referred to as reactivation) for a given alloy in a specific electrolyte, during which the amount of current resulting from the corrosion of the chromium-depleted regions surrounding the precipitated chromium carbide particles is measured. In a sensitised microstructure, the bulk of these particles is located at the grain boundaries and are particularly susceptible to corrosion in oxidising acids. Proposed national and international standards on EPR testing specify 0.5 M H_2SO_4 + 0.01 M KSCN at 30°C as the EPR test environment for sensitised austenitic stainless steels.

Three different forms of EPR test can be employed, designated as the single loop, double loop and reactivation ratio methods in Figure 19.20.

Single Loop EPR Test The single loop method requires the sample to be polished to a $1\ \mu\text{m}$ finish then passivated at +200 mV (S.C.E.) for 2 min following which the potential is decreased at $1.67\ \text{mV s}^{-1}$ until the corrosion potential of approximately -400 mV (S.C.E.) is reached. The reactivation process results in the preferential breakdown of the passive film in the

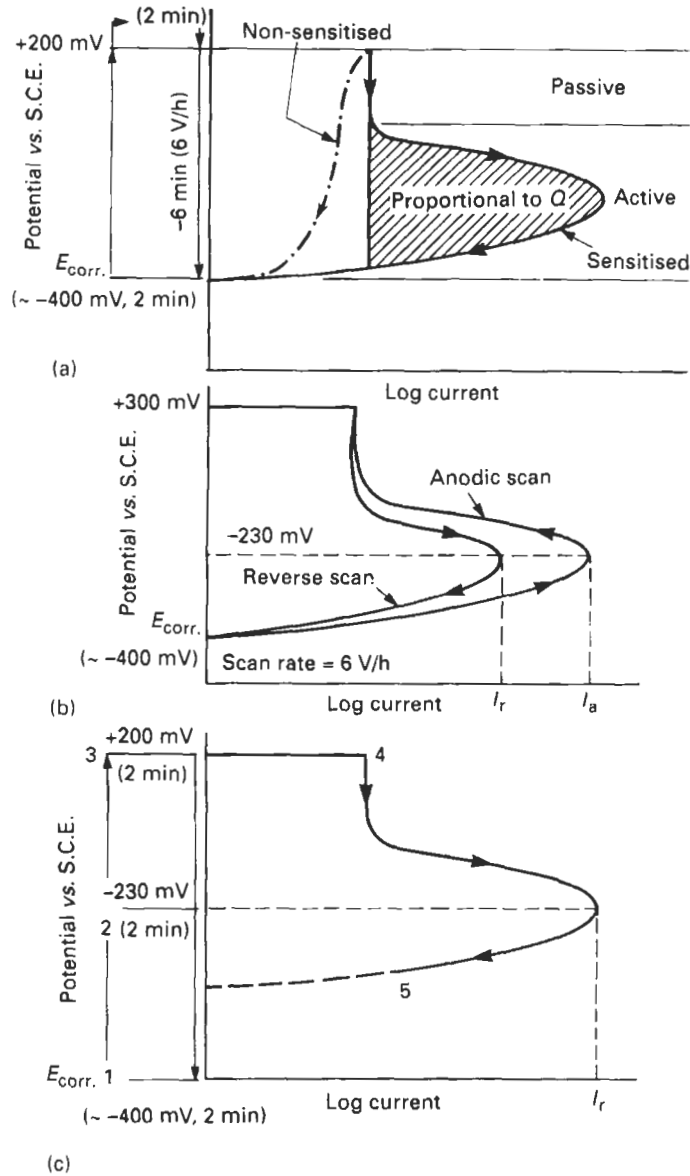


Fig. 19.20 Schematics of reactivation polarisation curves. (a) Single loop EPR test method, (b) double loop EPR test method and (c) reactivation ratio EPR test method

chromium-depleted grain boundaries of sensitised material and an increase in the current through the cell. The area under the E vs. $\log I$ curve (Fig. 19.20a) is proportional to the electric charge, Q , measured during the reactivation process. On non-sensitised materials, the current density during the reactivation step is very low because the passive film remains essentially intact. A measure of the degree of sensitisation is obtained by calculating the normalised charge, P_a , where:

$$P_a (\text{C cm}^{-2}) = Q/A$$

where Q = integrated charge during the reactivation scan, and A = grain boundary area ($5.1 \times 10^{-3} \exp 0.35G$, where G is the ASTM grain size at 100X magnification).

Pitting caused by the dissolution of non-metallic inclusions can increase the P_a value. Consequently, the microstructures of specimens with a high P_a value must be examined to identify the source of the elevated value. In general, P_a values below 0.10 are characteristic of unsensitised microstructures, while sensitisation is indicated if P_a exceeds 0.4. Single loop tests are sensitive to mild degrees of sensitisation but do not readily distinguish between medium and severely sensitised materials.

Double Loop EPR Test Details of this procedure are given in Japanese Industrial Standard JIS G 0580 (1986). The sample is ground to a 100 grit finish then placed in the test solution for about 2 min to establish the rest potential (about -400 mV (S.C.E.)) for AISI Types 304 and 304L stainless steel).

The sequence of polarisation steps is shown in Figure 19.20b. The surface is first polarised anodically from the corrosion potential to $+300$ mV (S.C.E.) at a rate of 1.67 mV s $^{-1}$. As soon as this potential is reached, the scanning direction is reversed and the potential is decreased at the same rate to the corrosion potential. The ratio of the maximum current in the reactivation loop, I_r , to that in the larger anodic loop, I_a , is used as a measure of the degree of sensitisation.

Reactivation Ratio EPR Test (Fig. 19.20c) This is a simpler and more rapid method than the single or double loop tests, and depends on the fact that the value of I_a determined during the anodic scan of a double loop test (which produces general dissolution without intergranular attack on sensitised material) is essentially the same for all AISI Type 304 and 304L steels.

The specimen is ground to a 100 grit finish then, after 2 min at the corrosion potential (about -400 mV (S.C.E.)), it is conditioned by a 2 min treatment at -230 mV (S.C.E.) in order to eliminate the need for polishing prior to the reactivation procedure. Passivation is then accomplished at $+200$ mV (S.C.E.) for 2 min after which the specimen is reactivated by scanning back to the corrosion potential at 1.67 mV/s. During this reactivation scan, the maximum current, I_r , is measured and is divided by the surface area as an indication of the degree of sensitisation.

EPR Tests for Ferritic Stainless Steels

Lee²⁰⁸ has demonstrated that in slightly modified forms the single loop EPR test can be used to quantify the degree of sensitisation in ferritic stainless steels. For AISI Types 430, 430Ti, 430Nb and 446 stainless steels, the test consists of passivating the specimen in deaerated 3 N H₂SO₄ solution at 30°C at $+400$ mV (S.C.E.) for 10 min, followed by reactivation at a scan rate of 250 mV min $^{-1}$. The EPR test for AISI Type 434 stainless steel requires a reactivating scan rate of 150 mV min $^{-1}$ (the other test conditions remaining unchanged). For AISI Type 444 stainless steel, the test is

conducted in deaerated 5 N H_2SO_4 solution at 30°C and involves passivation at $+400\text{ mV}$ (S.C.E.) for two min followed by reactivation at a scan rate of 100 mV min^{-1} .

Crevice Corrosion and Pitting

Crevice corrosion and pitting have been dealt with in some detail in Section 1.6, and it is not appropriate here to discuss the nature of the phenomena nor the methods that have been used to determine the mechanisms of these forms of localised attack. However, it should be noted that many of the methods of testing follow directly from the concepts that have been discussed in Section 1.6, and in particular the potentials E_b (the critical pitting potential) and E_p (the protection potential) have been investigated by a number of workers as possible criteria for the resistance of metals and alloys to pitting and crevice corrosion in service. It should also be noted that since crevice corrosion and pitting have similar mechanisms, and since the presence of a crevice is conducive to pitting of alloys that have a propensity, to this form of attack, it is appropriate to consider them under the same heading.

In general, the tests may be classified as follows:

1. Laboratory tests in which the specimen is immersed in a solution conducive to pitting such as an acidified FeCl_3 solution (redox potential above the critical pitting potential E_b).
2. Laboratory tests in which the specimen is anodically polarised in a chloride-containing solution to evaluate E_b and E_p .
3. Field tests in which the specimen (with or without a crevice) is exposed to the environment that it will encounter in service.

As far as tests for crevice corrosion are concerned all that is required is a geometrical configuration that simulates a crevice, which may be achieved in a variety of ways using either the metal itself or the metal and a non-metallic material. Figure 1.49 (Section 1.6) shows the testing arrangement used by Streicher²⁰⁹ to study the crevice corrosion of Cr-Ni-Fe alloys, in which two plastics cylinders are held on the two opposite faces of a sheet metal specimen by two rubber bands, thus providing three different types of crevice in duplicate. A simple method of testing for crevice corrosion produced by contact with different materials is to use a horizontal strip of the metal under study and place on its upper surface at intervals small piles of sand, small piles of sludge, pieces of gasket material, rubber, etc. More precise crevices can be produced by bolting together two discs of the metal, which are machined on the facing surfaces so that there is a flat central portion followed by a taper to the periphery of the disc, the flat central portion providing a very fine crevice and the tapered portion a coarser one²¹⁰.

Figure 19.21 shows the types of crevices used by Wilde²¹¹ for studying crevice corrosion and pitting of Cr-Ni-Fe alloys in the laboratory and in the field. Types 1 and 5 were used for anodic polarisation studies in nitrogen-saturated 1 mol dm^{-3} NaCl and in aerated 3.5 mass% NaCl, respectively, and it can be seen that attachment to the conducting lead is by means of a Stern-Makrides pressure gasket; Types 3 and 4 were used for field tests

in sea-water for periods up to $4\frac{1}{2}$ years; Type 2 was used for laboratory studies in which the specimens were immersed in acidified FeCl_3 ($108 \text{ g l}^{-1} \text{ FeCl}_3 \cdot 6\text{H}_2\text{O}$ with the pH adjusted to 0.9 with HCl).

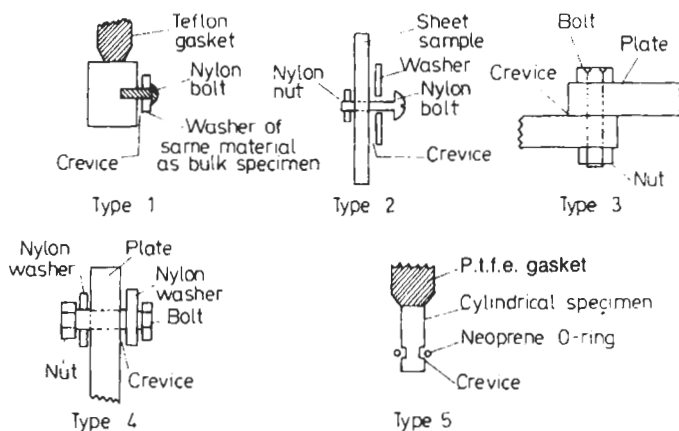


Fig. 19.21 Various types of crevices used for investigating crevice corrosion of Cr-Ni-Fe alloys (after Wilde²¹¹)

The value of electrochemical evaluation of the critical pitting potential as a rapid method of determining pitting propensity is controversial. France and Greene²¹² studied the pitting of a ferritic steel (Type 430) using a controlled potential test in $1 \text{ mol dm}^{-3} \text{ NaCl}$ and a conventional immersion test in oxygen-saturated $1 \text{ mol dm}^{-3} \text{ NaCl}$, but found that at the same potential (-0.17 to $0.09 \text{ V vs. S.C.E.}$) the corrosion rates were 390 and 5.2 mm/y , respectively. Similar studies were carried out on Zr using $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4 + 1 \text{ mol dm}^{-3} \text{ NaCl}$ for the controlled potential test and $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4 + \text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ for the immersion test, and again the former gave a much higher corrosion rate than the latter. France and Greene conclude that these two types of test give rise to significantly different results under identical test conditions. To explain the results obtained with the ferritic stainless steel they pointed out that during the controlled potential test the anodic reaction occurs at the metal's surface whereas the inter-dependent cathodic reaction takes place at the counter-electrode. Under these circumstances the M^{2+} ions produced anodically result in increased migration of Cl^- to maintain electroneutrality, and this in turn results in a higher concentration of Cl^- at the metal/solution interface with consequent increase in the rate of pitting. A similar situation does not arise during the immersion test where the anodic and cathodic sites are in close proximity and charge balance is maintained without migration of Cl^- from the bulk solution (see Fig. 19.39, Section 19.2).

Potentiostatic tests²¹³⁻²¹⁵ have been used and Wilde and Williams²¹³ in potentiokinetic studies of the critical breakdown potential of stainless steels (Types 430 and 304) in $1.0 \text{ mol dm}^{-3} \text{ NaCl}$, showed that the nature of the gas used to purge the solution has a pronounced effect on the value of E_b .

Table 19.5 Variation in E_b (V) for stainless steels in 1.0 mol dm^{-3} NaCl at 25°C with nature of dissolved gas (E_b vs. S.C.E.)^{*}

Gas	Type 430 stainless steel	Type 304 stainless steel
Hydrogen	-0.185	-0.050
Nitrogen	-0.130	-0.020
Argon	-0.100	+0.050
Oxygen	-0.035	+0.065

^{*} Data after Wilde and Williams^{2,3}

(Table 19.5). In particular, they have established that the presence of dissolved O_2 enhances passivity thus causing E_b to become more positive, and consider that this explains the failure of France and Greene to obtain accord between controlled potential tests in hydrogen-saturated chloride solutions and immersion tests in oxygenated chloride solutions at the same potentials.

Wilde and Williams²¹³ have used the redox system $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ in 0.1 mol dm^{-3} for their immersion tests, which for Type 403 stainless steel gives a corrosion potential of -0.100 V (vs S.C.E.); selection of this system was based on the premise that being large anions they would be less likely than dissolved O_2 to be involved in the adsorption processes that stabilise the passive state. Pitting occurred within 60 s, and equivalent tests on the same alloy conducted potentiostatically at -0.1 V (vs. S.C.E.) in hydrogen-saturated 1.0 mol dm^{-3} NaCl gave similar results. They conclude that these two tests give comparable results, but that extreme caution must be used in utilising E_b as an index of pitting, since its value is dependent upon environmental variables and in particular the nature of the dissolved gas in the corrodent. Wilde and Williams²¹⁶ have also shown that the critical pitting potential can be used to predict the behaviour of alloys exposed for long periods to sea-water or to industrial chemical environments.

In a subsequent paper Wilde²¹¹ pointed out that although E_b is qualitatively related to resistance of a material to breakdown of passivity and pit initiation, it is of questionable value in predicting performance when crevices are present. Wilde found that although the Fe-30Cr-3Mo alloy appeared to indicate total immunity to breakdown when tested anodically in 1 mol dm^{-3} NaCl and in the freely corroding condition in 10% FeCl_3 , it pitted within the crevice when an artificial crevice was present. Exposure in sea-water for a 16 month period showed that AISI Types 304 and 316 stainless steels and the Fe-30Cr-3Mo alloy all pitted to the same extent when a crevice was present, although the former two alloys are considered to be less resistant to pitting than the Fe-30Cr-3Mo alloy. Pourbaix, *et al.* have defined the protection potential E_p (see Section 1.6) as the potential below which no pits can initiate and pre-existing pits cannot propagate, since they are passive at that potential. However, Wilde using cyclic potentiodynamic sweeps at varying sweep rates has established that E_p is not a unique parameter and that it varies in a semi-logarithmic manner with the extent of localised attack produced during the anodic polarisation, i.e. E_p -log(extent of pit propagation) is linear. Thus at a sweep rate of 10 V h^{-1} , E_p was found to be -0.290 V (vs. S.C.E.) whilst it fell to a more negative value of

-0.410 V at the slower sweep rate of 1 V h^{-1} . This was explained by Wilde as being due to the chemical changes that occur in the growing pit by hydrolysis of corrosion products and by the increased migration of Cl^- ions. Since E_p is a variable that depends upon experimental procedures it cannot be used on its own as a criterion for protection against the propagation of pre-existing pits or crevices in an engineering structure. Wilde considers that a more useful parameter appears to be the 'difference potential' ($E_b - E_p$), which is used as a rough measure of the hysteresis loop area produced during the cyclic determination of E_b and E_p . The area of the hysteresis loop obtained in a potentiodynamic sweep using a specimen with an artificial crevice provides a measure of the resistance to crevice corrosion in service, i.e. the greater the area the lower the resistance. Figure 19.22 shows the linear relationship between the 'difference potential' and the mass losses of various stainless alloys containing an artificial crevice that have been exposed to sea-water for $4\frac{1}{2}$ years.

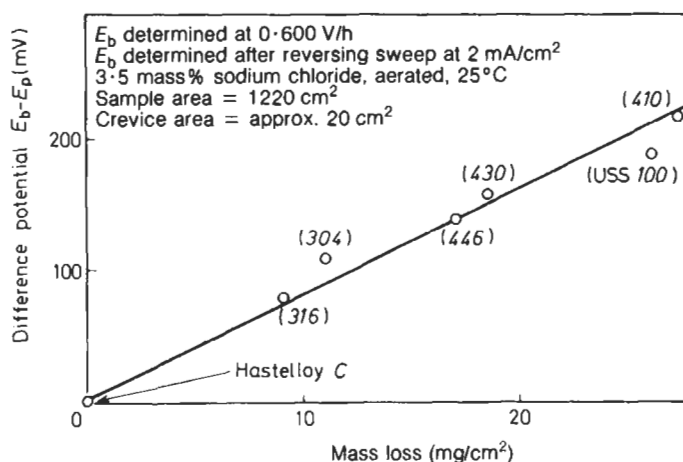


Fig. 19.22 Linear correlation between difference potential and the mass loss obtained for various stainless alloys containing a crevice, and after exposure to sea-water for $4\frac{1}{2}$ years (after Wilde²¹¹)

The above considerations show that although considerable advances have been made in developing laboratory controlled potential tests for evaluating crevice corrosion and pitting, the results must be interpreted with caution.

Guidance on crevice corrosion testing of iron-base and nickel-base stainless alloys in sea-water and other chloride-containing aqueous environments is given in ASTM G78:1989, while ASTM G61:1986 provides a standard test method for conducting cyclic potentiodynamic polarisation measurements for localised corrosion susceptibility (i.e. pitting and crevice corrosion) of iron-, nickel-, and cobalt-based alloys. Guidance on the selection of procedures for the identification and examination of pitting corrosion to determine the extent of its effect is available in G46:1976 (R1986).

Impingement Tests/Erosion Corrosion

The method most commonly used for testing condenser materials is the BNFMR May jet impingement test²¹⁷ in which small sections of tube, abraded to a standard finish, are immersed in sea-water and subjected to an underwater jet of sea-water containing air bubbles. However, at high velocities cavitation can occur in the water box in this test. An alternative design has been described to overcome this²¹⁸. Resistance to impingement attack is also assessed by the Brownsdon and Bannister test²¹⁹ in which a stream of air bubbles is directed onto the surface of the test specimens immersed in sea-water or sodium chloride solution. Special tests for resistance to corrosion under localised heat transfer conditions (hot-spot corrosion) have been described by Breckon and Gilbert²²⁰ and by Bem and Campbell²²¹, but temperature effects are usually ignored when comparing condenser tube materials.

Campbell²²² points out that in evaluating condenser tube materials a test apparatus is required that will include all the principal hazards likely to be encountered in service and should thus cater for the following conditions: impingement, slow moving water, heat transfer and shielded areas. Furthermore, the internal surfaces should not be abraded, as in the jet impingement test, but should be tested in the 'as-manufactured' condition, particularly in view of the deleterious effect of carbon films produced during manufacture (see Sections 1.6 and 4.2). LaQue has pointed out the importance of specimen area in impingement tests²²³.

The general arrangement of the apparatus is shown in Fig. 19.23. It accommodates 10 vertical 200 mm lengths of condenser tube spaced equally around a 125 mm diameter circle. Water enters the bottom of each tube through an inlet nozzle (Part No. 6 in Fig. 19.23) which fits inside the tube and also locates it. The nozzle has a 5 mm diameter blind hole up the centre connecting with a 2.4 mm diameter hole, set at 45° to the vertical, through which the water emerges at a velocity of 10 m s⁻¹ to impinge on the wall of the tube. The water then rises up through the tube at a mean velocity of 0.1 m s⁻¹ (in a 22–24 mm dia. condenser tube) and leaves through an outlet nozzle (Part No. 1) fitted into the top end of the tube. Half the length of each outlet nozzle has a 2° taper on the outside to provide a reproducible annular crevice between it and the inside of the condenser tube. Neoprene 'O'-rings (Part No. 3) provide seals between the tube and the top and bottom nozzles, and the tubes are held in place by a common clamping plate (Part No. 2) at the top. The 10 inlet nozzles are fed with water through a distributor (Parts Nos. 7, 8 and 15) of the design used in the May jet impingement apparatus, which ensures equal distribution of water between them. The distributor and nozzles are all of non-metallic materials. The part of each test piece between 40 and 65 mm from the top is fine-machined externally to fit a semi-circular notch in a 15 mm thick brass heater block (Part No. 4), the tubes being held in contact with the block by a circumferential clip to ensure efficient and equal heat transfer between the block and each tube. The diameter of the inlet and outlet nozzles and that of the semi-circular notches in the heater block are made to suit the size of condenser tube to be tested.

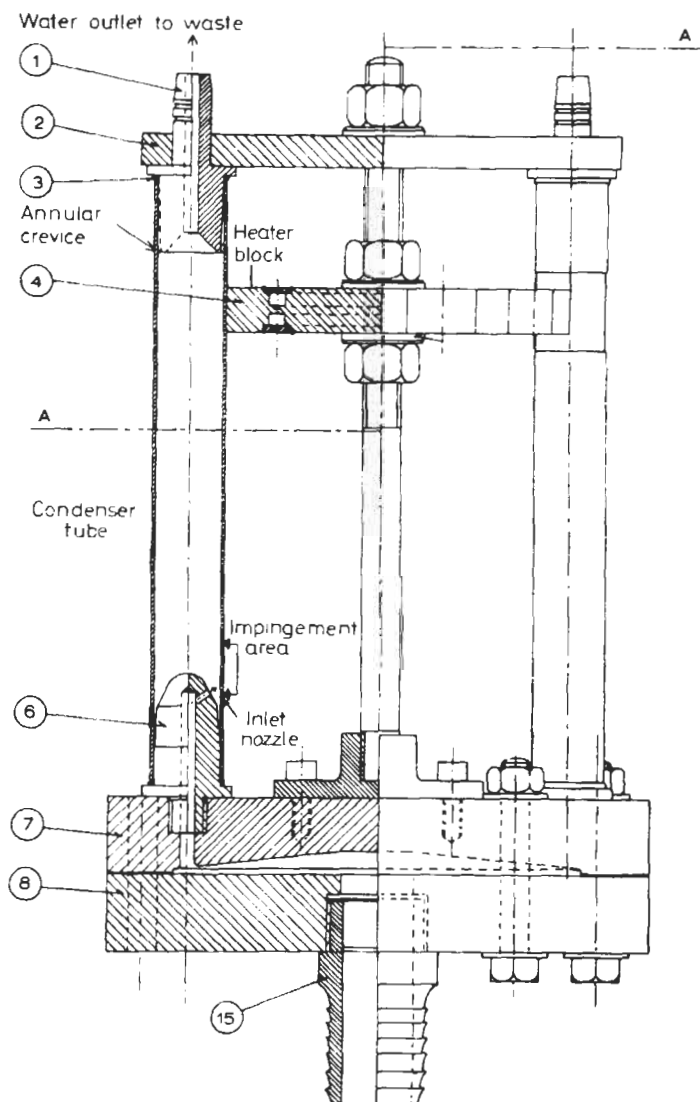


Fig. 19.23 Campbell test apparatus for determining the various forms of attack that condenser-tube materials are subjected to in service (after Campbell²²²)

The common heater block shown in Fig. 19.23 can itself be subject to corrosion leading to different heat transfer conditions for different tubes, and in some later versions of the apparatus individual short heating jackets are used for each tube, which are heated with oil from either a steam-heated or electrically heated heat exchanger. This modification not only avoids corrosion problems but also obviates the necessity to machine a length of the outside of each tube to fit the semi-circular notches in the single heater block. The oil flow is adjusted to give an oil temperature of 95°C at each outlet.

The test usually lasts 8 weeks, after which the tubes are sectioned longitudinally and their interiors inspected for accumulated deposits. Loose deposits are then removed by washing in water and the internal surfaces are examined for impingement attack, pitting and blistering or flaking of the corrosion-product film, using a low-power binocular microscope. After cleaning the section in 10% H_2SO_4 , the depth of impingement attack, pitting or other localised corrosion, is determined. Observations and measurements are recorded for each of the following five areas of the section: (a) impingement area opposite the inlet nozzle where water velocity and turbulence are greatest, (b) the slow-moving cold water area from the impingement area upwards to the heated area, (c) the heated area including the heat-transfer area itself and the warm water area above and (d) the two annular crevices formed between the tapered portions of the cold-water inlet and warm-water outlet nozzles and the tube wall.

The Campbell apparatus is cheap to construct and easy to use, and can be installed on site to assist the selection of condenser or heat-exchanger tube materials, or to monitor changes in the corrosivity of the cooling water. The information that it provides on the various forms of attack is more comprehensive than that of any other existing apparatus for corrosion testing condenser tubes, and it is therefore particularly suitable also for assessing new materials or the effect of surface conditions arising from changes in manufacture.

Impingement and erosion-corrosion forms of attack will usually be intensified by the presence of solid particles in the fluid. Variations of the jet test have been proposed to take this effect into account²²⁴.

Test equipment for the study of erosion-corrosion by liquids with sand content, as met in formation waters in oil and gas production, has been described by Kohley and Heitz²²⁵.

Corrosion Fatigue

The simultaneous action of alternating stresses and corrosion usually has a greater effect than when either is operating separately, and in this respect corrosion fatigue is analogous to stress-corrosion cracking. The important factors in corrosion fatigue (see Section 8.6) include the following:

1. environmental conditions;
2. magnitude of the alternating stress;
3. magnitude of mean stress.
4. frequency of reversal of the stress.
5. load-versus-time waveform;
6. characteristics of the metal.

Depending on the intended purpose, corrosion fatigue tests can be conducted on smooth, notched or pre-cracked specimens as well as on components and parts joined by welding. Because of the time-dependent nature of corrosion processes, it is essential that the mechanical variables employed during corrosion fatigue testing, including cyclic frequency and load-versus-time waveform, as well as the chemical and electrochemical conditions, are relevant to the intended application. For example, it is unlikely that data generated in a laboratory test at a frequency of 10 Hz would be applicable

for predicting corrosion fatigue behaviour in a structure which is cycled at 0.1 Hz.

Laboratory corrosion fatigue tests can be classified as either cycles to failure (crack initiation) or crack propagation tests²²⁶. Cycles to failure tests employ plain or notched specimens to provide data on the intrinsic corrosion fatigue crack initiation behaviour of a metal or alloy. Crack propagation tests use pre-cracked specimens to provide information on the threshold conditions for the propagation of pre-existing defects by corrosion fatigue and on the rates of corrosion fatigue crack growth.

It is often difficult to conduct laboratory tests in which both the environmental and stressing conditions approximate to those encountered in service. This applies particularly to the corrosive conditions, since it is necessary to find a means of applying cyclic stresses that will also permit maintenance around the stressed areas of a corrosive environment in which the factors that influence the initiation and growth of corrosion fatigue cracks may be controlled. Among these factors are electrolyte species and concentration, temperature, pressure, pH, flow rate, dissolved oxygen content and potential (free corrosion potential or applied).

For tests on plain or notched specimens, a simple approach can be to use a conventional Wöhler rotating cantilever beam modified so as to permit the specimen to be brought into contact with the corrodent. This may be achieved by surrounding the specimen with a cell through which the corrosive solution is circulated or by applying it by a pad²²⁷, wick²²⁸ or drip feed²²⁹. Four-point loading or push-pull machines can be used in a similar way, and have the advantage over the Wöhler machine when testing plain specimens that the length of the test-piece between the two points of loading is subjected to an approximately uniform stress.

Rawdon²³⁰ used flat specimens that were subjected to repeated flexure while they were being immersed periodically in the corrosive solution. Kenyon²³¹ used a rotating wire specimen in the form of a loop, the upper part of which was attached to the motor whilst the lower part of the loop passed through the corrodent, and a somewhat similar device was developed by Haigh-Robertson and used in several studies^{232, 233}. Gough and Sopwith^{234, 235} used this machine in their studies, the corrodent being applied as a spray.

Figure 19.24 shows a slow fatigue machine²³⁶ that has been developed to study the performance of welded butt and fillet joints for steels used in the construction of North Sea oil drilling-rigs; the bending stress and frequency have been selected to simulate the forces produced by the wave motion. The specimens, 1500 × 100 × 12.5 mm with the weld 25 cm from the base, are clamped at the lower end and the stress is applied as a variable bending moment at the upper end by rams. The rams, which are attached to a sliding frame, are activated by a pneumatic cylinder that can be automatically programmed for stroke and frequency and the stress level is monitored by strain gauges. The maximum amplitude of stress is 150 mm, the stress range is up to 300 MN m⁻² and the frequency can be varied from 1 cycle/2 s to 1 cycle/20 s. The corrodent is artificial sea-water, and provision is made for studying the effect of cathodic protection by means of Zn anodes.

Hoepfner²³⁷ pointed out that until the early 1970s, most investigators conducted fatigue tests utilising rotating bending, flat plate bending or

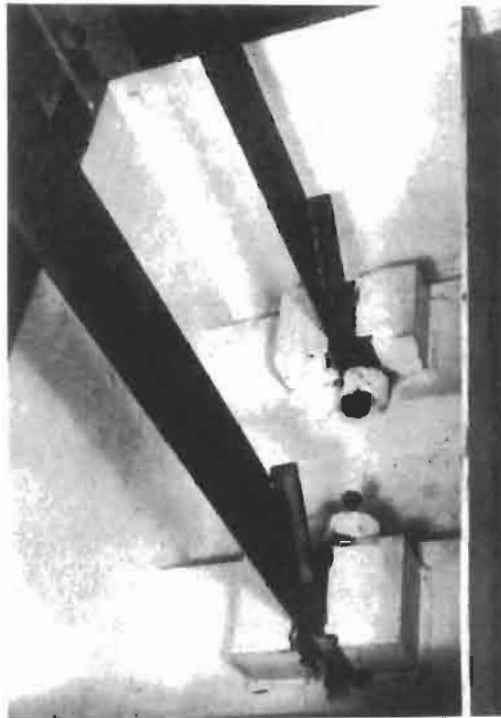
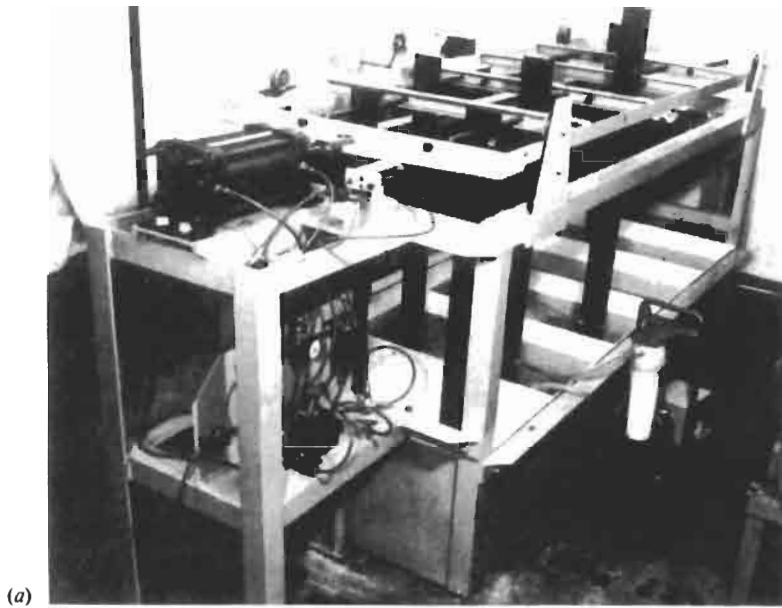


Fig. 19.24 (a) Rig for a laboratory study of the corrosion fatigue of welded joints in sea-water and (b) view of test-pieces showing welded joint (after Jarman *et al.*²³⁶)

torsion-type loading configurations, which have the disadvantage that tests at positive or negative mean-stress values are difficult to achieve. In addition, the rotating bending and flat-plate-bending tests create complex stress states upon crack initiation, e.g. a shifting neutral axis. For these reasons, axial load fatigue machines, as recommended by the ASTM Committee E9, are preferred.

The results obtained from the tests described above are presented in the form of the conventional S - N curve, where S is the stress and N the number of cycles to cause fracture. Curves of this type are obtained for the metal in air and for the metal in the corrodent, and comparison provides information on the effect of the corrosive environment on the fatigue life. Hoepfner points out that even though the S - N curve for either notched or unnotched specimens may be useful for certain applications it cannot always be employed to evaluate the effect of the environment on the fatigue life. This is because in some materials the inherent metallurgical and fabrication discontinuities, which may be undetectable by non-destructive testing will be so large that the only factor of engineering significance will be the rate of propagation of a crack from the initial defect, i.e. the fatigue-crack propagation rate may play the dominant rôle in the useful life of the component. For this reason it is important to conduct fatigue crack growth tests on pre-cracked specimens, and the data are then presented in the form of curves showing crack growth rate, da/dN , vs. stress intensity factor range, ΔK .

The NACE publication *Corrosion Fatigue*²³⁷ gives a comprehensive account of all aspects of the subject, and in this work a review of the application of fracture mechanics for studying the phenomenon has been presented by McEvily and Wei²³⁸, whilst Kitagawa²³⁹ has given a detailed account of crack propagation in unnotched steel specimens. This work should be consulted for details of testing and interpretation of results.

Special requirements for fatigue testing in aqueous environments are addressed in the Annexe to ASTM E647:1986a 'Standard Test Method for Measurement of Fatigue Crack Growth Rates'.

Cavitation—erosion

The phenomenon and mechanisms of cavitation-erosion have been considered in Section 8.8 and here it is only necessary to consider laboratory test methods that have been designed to simulate conditions that prevail in practice and which may be used to evaluate the performance of materials.

In considering these tests it should be remembered that the phenomenon of cavitation-erosion is often accompanied by corrosion effects and that a synergistic effect may operate between the mechanically and chemically induced forms of attack. In fact the term cavitation-erosion-corrosion may often be more applicable in describing the requirements of a test procedure. The subject has recently been discussed by Wood *et al.*²⁴⁰.

The methods used have been classified by Lichtman, *et al.*²⁴¹ as follows:

1. High-velocity flow.
 - (a) Venturi tubes.
 - (b) Rotating discs.
 - (c) Ducts containing specimens in throat sections.

2. High-frequency vibratory devices.
 - (a) Magnetostriction devices.
 - (b) Piezoelectric devices.
3. Impinging jet.
 - (a) Rotating specimens pass through continuous, stationary jets or droplets.
 - (b) Stationary specimens exposed to high-speed jet or droplet impact.

All tests are designed to provide high erosion rates on small specimens so that the test can be conducted in a reasonable time, and although vibratory and high-velocity jet methods may not simulate flow conditions they give rise to high-intensity erosion and can be used, therefore, for screening materials.

The essential component of many high-velocity flow rigs is a Venturi-type section in which cavitation occurs in the low-pressure high-velocity region created by the Venturi throat. Typical of this type is the double-weir arrangement used by Schroter²⁴², but since this technique requires very large volumes of water it is not readily adaptable to laboratory use. Hobbs²⁴³ and others have used a uniform-area rectangular-cross-section duct in which a cylinder of small diameter is inserted; cavitation occurs in the wake of the cylinder, which may be used as the test specimen or the specimen may be set in the side wall of the duct near the cylinder. The cavitation intensity will be dependent on the configuration of the test section and the velocity, pressure, temperature, viscosity, surface tension, corrosivity, gas content and density of the liquid.

Devices in which cavitation is achieved by vibrating a test specimen at high frequencies are often used. The original apparatus was developed by Gaines²⁴⁴, and was adapted for cavitation-erosion studies by Hunsaker and Peters as described in the paper by Kerr²⁴⁵ it has been used also by Beeching²⁴⁶, Rheingans²⁴⁷ and Leith, *et al.*²⁴⁸. In this method cavitation is produced by attaching the specimen to the vibrating source or by means of a partially immersed probe vibrating axially at a high velocity and low amplitude and placed close to the test specimen. Although originally magnetostriction oscillators were used²⁴⁴ these have now been largely superseded by piezoelectric oscillators, which are more efficient. The apparatus consists basically of a conventional ultrasonic generator, a piezoelectric transducer and a resonating horn or probe, and the majority of tests are carried out at a frequency of 20 kHz.

Originally the test specimen was fastened to the end of the ultrasonic probe, and this is still specified in ASTM D2939-71 which describes a method of testing aluminium in antifreeze solution. However, this arrangement also subjects the test-piece to high alternating stresses as a result of the high accelerations associated with vibration at ultrasonic frequencies, which may be overcome by using a stationary test-piece and locating it immediately below a dummy tip placed on the end of the ultrasonic probe.

Vibratory test apparatuses are relatively cheap to build and run, and have low power consumption, while flow rigs are bulky, expensive to build and run, and have high power consumptions but have the advantage that they simulate more closely practical conditions of hydrodynamic cavitation. On the other hand, the damage rate is higher in the vibratory tests than in the

flow test, although whether this is advantageous depends on the objectives of the test. A further criticism of the vibratory test is that the mechanical component is over-emphasised in relation to the effect produced by corrosion. For this reason Plesset²⁴⁹ uses a technique in which cavitation is intermittent with short bursts of vibration followed by longer static periods, which significantly increases the erosion rate of materials with poor corrosion resistance but has little effect on materials with good corrosion resistance. Tests of this type have distinguished readily between materials having the same hardness but different resistances to corrosion, and between corrosive and non-corrosive solutions.

Figure 19.25 shows an apparatus for studying cavitation-corrosion using the magnetostriction principle for vibration. A nickel tube is made the core of a magnetic field tuned to the natural frequency of the tube assembly, and since nickel changes its length as it is magnetised and demagnetised it will vibrate with the frequency of the magnetising current. The specimen under test vibrates with the nickel tube, and a commonly used frequency is 6 500 Hz with an amplitude of 0.008–0.009 cm. Damage is increased by the amplitude of vibration, and the more resistant the material the greater the amplitude to achieve substantial attack. Increase in temperature decreases damage by increasing the vapour pressure within the cavitation bubbles, thus reducing the force of their collapse, but in opposition to this effect is the increased damage resulting from the lower solubility of gases which cushion the collapse of the cavitation bubbles. Consequently, under many circumstances damage reaches a maximum at a test temperature of about 46–52°C.

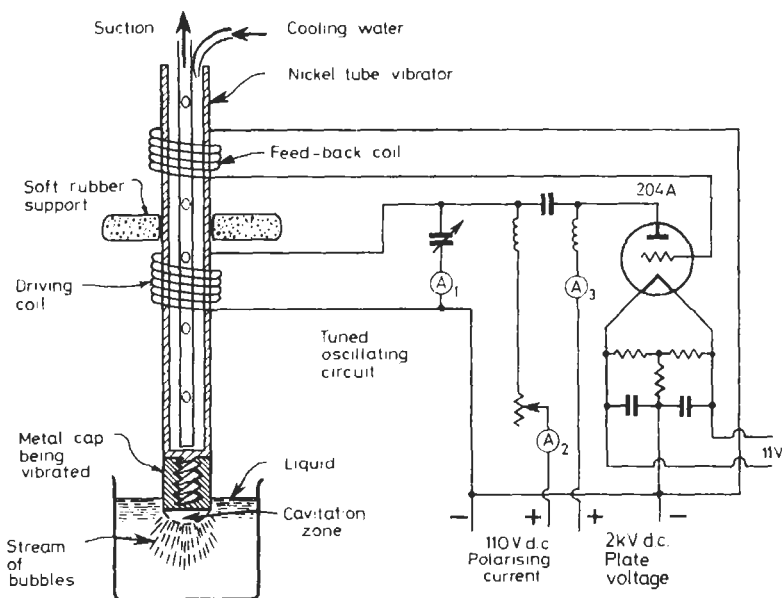


Fig. 19.25 Vibratory cavitation-erosion test using magnetostriction

Assessment of cavitation-erosion is based on mass loss and the results are expressed as curves showing cumulative mass (or volume) loss vs. the time of the test. Eisenberg, *et al.*²⁵⁰ have expressed the cumulative mass loss plot on the basis of the rate vs. time curve as follows:

1. Incubation zone (little or no mass loss).
2. Accumulation zone (increasing rate to a maximum).
3. Attenuation zone (decreasing loss rate to a steady-state value).
4. Steady-state zone (loss rate at a constant value).

It has been proposed that evaluation of the resistance of materials, or the study of experimental variables, should be based on the results obtained for the attenuation zone. Other methods of assessment have been proposed by Hobbs²⁵¹, and by Plesset and Devine²⁵².

Examples of various vibratory test procedures for studying cavitation-erosion of metals in inhibited engine coolants have been given in an ASTM Special Technical Publication²⁵³⁻²⁵⁵.

Fretting Corrosion

The deterioration of surfaces that occurs when parts supposedly tightly fitted together nevertheless move slightly relative to each other in some sort of cycle under load is called *fretting* corrosion (*see* Section 8.7). With ferrous materials the characteristic corrosion product is a finely divided cocoa-coloured oxide. The general state of knowledge of the subject was reviewed in a symposium on fretting corrosion held by the ASTM in 1952²⁵⁶ and more recently by Waterhouse^{257, 258}.

Several techniques for reproducing fretting corrosion have been used. All involve some means for controlling contact pressure, and for achieving and measuring small-amplitude cyclic motion or slip between the contacting surfaces; some control of the environment, particularly moisture which has a considerable effect on the extent of damage, is also desirable. Fink²⁵⁹ used an Amsler wear machine. Another early series of tests on fretting corrosion arose from a study of the bottom bearings of electricity meters by Shotter²⁶⁰. Tomlinson, Thorpe and Gough²⁶¹ adapted a Haigh alternating-stress machine by which annular specimens were pressed together under load while being subjected to vibration to achieve the required slip. These investigators also used apparatus in which a specimen having a spherical surface was moved cyclically through a small amplitude while in contact under load with a plane surface. A further modification involved an upper specimen machined to provide an annulus which was oscillated under load in contact with a lower plane specimen. A similar technique was used by Wright²⁶². The area of damage was measured optically and the maximum depth of damage was calculated by carefully lapping the lower surface and determining the change in mass. In addition, the amount of oxidised debris was determined chemically.

Uhlig, Tierney and McClellan²⁶³ measured fretting damage by mass loss of recessed 25.4 mm diameter steel cylinders subjected to radial oscillating motion. The specimens were loaded pneumatically, frequency was varied,

and slip was adjusted up to 0.020 mm. Mass loss was determined after debris had been removed by pickling the specimens in inhibited acid.

McDowell²⁶⁴ used a set-up which took advantage of the elastic modulus of one of the test materials to provide a definite deflection subject to control. A rotating-beam fatigue-testing machine was used to produce an alternating compressive and tensile deflection on the surface of the rotating specimen. A sliding specimen slipped back and forth on the rotating specimen as the outer fibres were strained alternately in tension and compression in proportion to the extent of deflection of the rotating specimen.

Horger²⁵⁶ undertook rotating-beam fatigue tests of press-fitted assemblies using specimens as large as 305 mm diameter shafts.

Warlow-Davies²⁶⁵ used a technique in which specimens were subjected to fretting corrosion and then tested in fatigue to show the effect of fretting damage in lowering resistance to fatigue.

Herbeck and Strohecker²⁵⁶ used machines designed particularly for comparing the merits of lubricants in preventing fretting corrosion of anti-friction bearings. One provided for both oscillating conditions and combination radial and thrust loads to simulate service. Another was concerned primarily with thrust bearings and correlated satisfactorily with the radial load tester.

An interesting approach involved microscopic observation of fretting corrosion; a glass slide mounted on the stage of a microscope was used for the bearing surface which pressed against a spherical specimen being vibrated by a solenoid²⁶⁶.

Other testing machines and techniques have been described by Gray and Jenny²⁶⁷, Villemeur²⁶⁸, Wright^{269, 270}, Barwell and Wright²⁷¹, Field and Waters²⁷², and Waterhouse²⁷³.

Corrosion Testing in Liquid Metals and Fused Salts*

Liquid metals have high heat capacities and heat transfer coefficients, and these and other properties make them attractive as coolants for high-temperature nuclear reactors and as heat-transfer and working fluids in power-generation systems that operate in conjunction with nuclear reactors. However, austenitic cladding and ferritic structural steels can suffer rapid corrosion when exposed to liquid metals at high temperatures (e.g. in liquid sodium at temperatures above 600°C or in liquid Pb-17at%Li eutectic alloy at temperatures above 500°C). Similar corrosion processes affect numerous solid/liquid metal systems, including molybdenum in liquid sodium or lithium, stainless steel in liquid aluminium, platinum in liquid sodium and carbon steel in liquid zinc.

Corrosion by liquid metals is usually controlled by diffusion processes in the solid and liquid phases and, unlike aqueous corrosion, does not generally involve galvanic effects, and, even where electrochemical phenomena are known to occur, it has not, in general, been demonstrated that they have been responsible for a significant portion of the corrosion observed²⁷⁴. In

* See also section 2.10.

fused salts, there is evidence that electrochemical factors are involved^{275, 276}. Nevertheless, the corrosion process in relation to liquid metals and fused salts may conveniently be considered under one of the following processes which do not directly include electrochemical factors: 1. chemical reaction; 2. simple solution; 3. mass transfer; 4. impurity reactions. Several of the above processes may be involved in a single corrosion reaction, but for simplicity they will be treated separately.

Chemical reaction This involves the formation of distinct compounds by reaction between the solid metal and the fused metal or salt. If such compounds form an adherent, continuous layer at the interface they tend to inhibit continuation of the reaction. If, however, they are non-adherent or soluble in the molten phase, no protection will be offered. In some instances, the compounds form in the matrix of the alloy, for example as grain-boundary intermetallic compound, and result in harmful liquid metal embrittlement (LME) although no corrosion loss can be observed.

Simple solution The liquid phase may simply dissolve the solid metal or the liquid may go into solid solution with the metal to form a new phase. In some instances, only a single constituent of an alloy will dissolve in the liquid phase; in this case, a network of voids extending into the metal will result, with obvious deleterious effects.

Mass transfer This phenomenon manifests itself as the physical transport of a metal from one portion of the system to another, and may occur when there is an alloy compositional difference or a temperature gradient between parts of the unit joined by the flowing liquid phase. An exceedingly small solubility of the metal component or corrosion product in the molten metal or salt appears sufficient to permit mass transfer to proceed at a fairly rapid pace.

Impurity reactions Small amounts of impurities in the liquid phase or on the surface of the solid metal may result in the initiation of attack or in increased severity of attack by one of the mechanisms just outlined.

In general, it is fair to state that one of the major difficulties in interpreting, and consequently in establishing definitive tests of, corrosion phenomena in fused metal or salt environments is the large influence of very small, and therefore not easily controlled, variations in solubility, impurity concentration, temperature gradient, etc.²⁷⁷. For example, the solubility of iron in liquid mercury is of the order of 5×10^{-5} at 649°C, and static tests show iron and steel to be practically unaltered by exposure to mercury. Nevertheless, in mercury boiler service, severe operating difficulties were encountered owing to the mass transfer of iron from the hot to the cold portions of the unit. Another minute variation was found substantially to alleviate the problem: the presence of 10 ppm of titanium in the mercury reduced the rate of attack to an inappreciable value at 650°C; as little as 1 ppm of titanium was similarly effective at 454°C²⁷⁸.

In the case of the alkali metals, impurities such as oxygen and carbon can have a significant effect on the corrosion of steel and refractory metals.

Borgstedt and Frees²⁷⁹ have shown that for the corrosion of both stabilised and unstabilised austenitic stainless steels in flowing liquid sodium at 700°C there is an almost linear dependence of the corrosion constant, k , on the oxygen content of the sodium, as follows:

$$\log k = -5.6637 + 0.919 \log [\text{O}] \quad \dots (19.17)$$

where k is in $\text{mg cm}^{-2} \text{h}^{-1}$ and $[\text{O}]$ is in ppm). Barker *et al.*²⁸⁰ have demonstrated that oxygen exerts a similarly deleterious effect on the corrosion of AISI Type 316 austenitic stainless steel in liquid Pb-17Li eutectic by increasing the depth of the ferritic corrosion layer and the extent of chromium depletion within the layer.

The effect of carbon on the corrosion of stainless steels in liquid sodium depends upon the test conditions and the composition of the steels²⁷⁹. Stabilised stainless steels tend to pick up carbon from sodium, leading to a degree of carburisation which corresponds to the carbon activity in the liquid metal. Conversely, unstabilised stainless steels suffer slight decarburisation when exposed to very pure sodium. The decarburisation may promote corrosion in the surface region of the material²⁸¹ and, under creep rupture conditions, can lead to cavity formation at the grain boundaries and decreased strength.

Testing

As in all corrosion testing, the procedure which most nearly duplicates the conditions anticipated in service will provide the most satisfactory and useful information for those aspects of corrosion under consideration here. In fact, in view of the extraordinary sensitivity of fused metal and salt corrosion phenomena to minute variations in operating conditions and purity of components, as already discussed, failure to reproduce these conditions with considerable accuracy may well make any test results completely unrealistic and worthless. In all of the following, then, it should be understood, if not explicitly stated, that all extraneous matter must be carefully excluded from the system and that only materials closely simulating those to be employed in service (including prior history and surface preparation of the metals) should be used. Other factors affecting the corrosion in liquid metals and fused salts include the heat flux of the corroding surface, the volume of liquid to the surface area of the solid, the heat flux of the corroding surface and the liquid flow rate. If, however, screening tests to establish the compatibility of a relatively large number of metals with a given molten metal or salt are to be run, it is often useful to commence with static tests even though the ultimate application involves a dynamic system. This is desirable because static tests are comparatively simple to conduct and interpret, and considerably more economical to operate, and because experience has shown that a metal which fails a static test is not likely to survive the more severe dynamic test²⁸². Static tests have been used by Grabner *et al.*²⁸³ to investigate the compatibility of metals and alloys in liquid Pb-Li eutectic at temperatures up to 650°C.

Static Tests Ideally, a static test would consist of immersing a test sample in the liquid medium held in an inert container under isothermal conditions.

Tests in mercury, for example, may be contained in glass at temperatures of several hundred degrees²⁸⁴. Unfortunately, at the higher temperatures and with the aggressive metals and salts of interest there are few readily available inert container materials, and results will often vary according to the nature of the container. The most satisfactory solution is to make the container of the same material as the test sample, or even in some cases to let it be the sample. Klueh used small capsules for determining the effect of oxygen on the compatibility of Nb and Ta with sodium²⁸⁵ and potassium²⁸⁶. For the Nb-K tests the Nb specimen was approximately $2.5 \times 1.4 \times 0.1$ cm and was contained in a Nb capsule surrounded by another capsule of welded Type 304 stainless steel. It was demonstrated that the oxygen concentration, added as K_2O , markedly increased the solubility of the Nb in the molten K. DiStefano²⁸⁷ studied the interaction of Type 316 stainless steel with Nb (or Nb-1Zr) in Na and Na-K by exposing tensile specimens of Nb (Nb-1Zr) to the liquid metal in a stainless steel container. Carbon and nitrogen from the stainless steel were transferred to the Nb resulting in carbide-nitride at the surface and diffusion of nitrogen into the metal, thus producing an increase in tensile strength and a decrease in ductility. Close control of temperature is also essential if reproducible results are to be obtained, because of differential solubility as a function of temperature. For example, the corrosion rate for Cu-Bi at $500 \pm 5.0^\circ\text{C}$ is several times its rate at $500 \pm 0.5^\circ\text{C}$ ²⁸⁸.

Refluxing capsules In systems where a liquid metal is used as the working fluid, the liquid is converted to vapour in one part of the system whilst the converse takes place in another, and the effect of a boiling-condensing metal on the container materials is most readily studied in a refluxing capsule. DiStefano and De Van²⁸⁹ used a system in which the lower part of the capsule was surrounded by a heating coil whilst the upper part was water cooled. Specimens were inserted in the upper part of the capsule and thus exposed to the condensing vapour, the rate of condensation being controlled by the water flow rate.

When close control of purity is essential it may be necessary to assemble the test specimens in a dry box under an inert atmosphere and to weld the containers shut under inert gas or vacuum before placing on test. With some environments even the small amount of oxygen and moisture adsorbed on the component surfaces will significantly affect the test results. In one laboratory this problem was eliminated by maintaining within the dry box a container of molten sodium at 250°C ²⁸²—a rather cumbersome procedure, but one which emphasises again the importance of purity.

Static test results may be evaluated by measurement of change of mass or section thickness, but metallographic and X-ray examination to determine the nature and extent of attack are of greater value because difficulty can be encountered in removing adherent layers of solidified corrodent from the surface of the specimen on completion of the exposure, particularly where irregular attack has occurred. Changes in the corrodent, ascertained by chemical analysis, are often of considerable value also. In view of the low solubility of many construction materials in liquid metals and salts, changes in mass or section thickness should be evaluated cautiously. A limited volume of liquid metal could become saturated early in the test and the reaction would thus be stifled when only a small corrosion loss

has occurred, whereas with a larger volume the reaction would continue to destruction^{288, 290}.

Dynamic Tests Various tests have been devised to study the effects of dynamic conditions and one of the simplest tests is to use a closed capsule that contains a sample at each end and is partially filled with the liquid metal or salt²⁹¹. A temperature gradient is maintained over the length of the tube, and the capsule is rocked slowly so that the liquid metal passes from one end to the other. After the test, the extent of mass transfer is determined from the two specimens placed at each end of the capsule. Tests of this type are useful to establish whether thermal-gradient mass transfer (or concentration-gradient mass transfer if dissimilar metals are incorporated in the system) will occur, but although the method is useful for screening purposes, the dynamic nature of the heating and cooling cycles prevents a rigorous analysis of mass transfer in terms of time and temperature.

High velocity effects can also be studied in spin tests using cylindrical specimens of the solid metal and rotating them at high velocities in an isothermal-metal bath. Although strictly speaking only a single alloy should be tested at a time, it is generally satisfactory to include a variety of alloys since the velocity effects become manifest at considerably shorter times than does mass transfer.

Kassner²⁹² used a rotating disc, for which the hydrodynamic conditions are well defined, to study the dissolution kinetics of Type 304 stainless steel in liquid Bi-Sn eutectic. He established a temperature and velocity dependence of the dissolution rate that was consistent with liquid diffusion control with a transition to reaction control at 860°C when the speed of the disc was increased. The rotating disc technique has also been used to investigate the corrosion stability of both alloy and stainless steels in molten iron sulphide and a copper/65% calcium melt at 1220°C²⁹³. The dissolution rate of the steels tested was two orders of magnitude higher in the molten sulphide than in the metal melt.

Loop Tests Loop test installations vary widely in size and complexity, but they may be divided into two major categories: (a) thermal-convection loops; and (b) forced-convection loops. In both types, the liquid medium flows through a continuous loop or harp mounted vertically, one leg being heated whilst the other is cooled to maintain a constant temperature across the system. In the former type, flow is induced by thermal convection, and the flow rate is dependent on the relative heights of the heated and cooled sections, on the temperature gradient and on the physical properties of the liquid. The principle of the thermal convective loop is illustrated in Fig. 19.26. This method was used by De Van and Sessions²⁹⁴ to study mass transfer of niobium-based alloys in flowing lithium, and by De Van and Jansen²⁹⁵ to determine the transport rates of nitrogen and carbon between vanadium alloys and stainless steels in liquid sodium.

The thermal-convection loops are limited to flow velocities up to about 6 cm s⁻¹. Where higher velocities are required, the liquid must be pumped, either mechanically or electromagnetically; the latter is usually preferred as it avoids the problem of leakage at the pump seal. Basically, these forced-convection systems²⁹⁵⁻²⁹⁸ consist of (a) a hot leg, where the liquid metal is

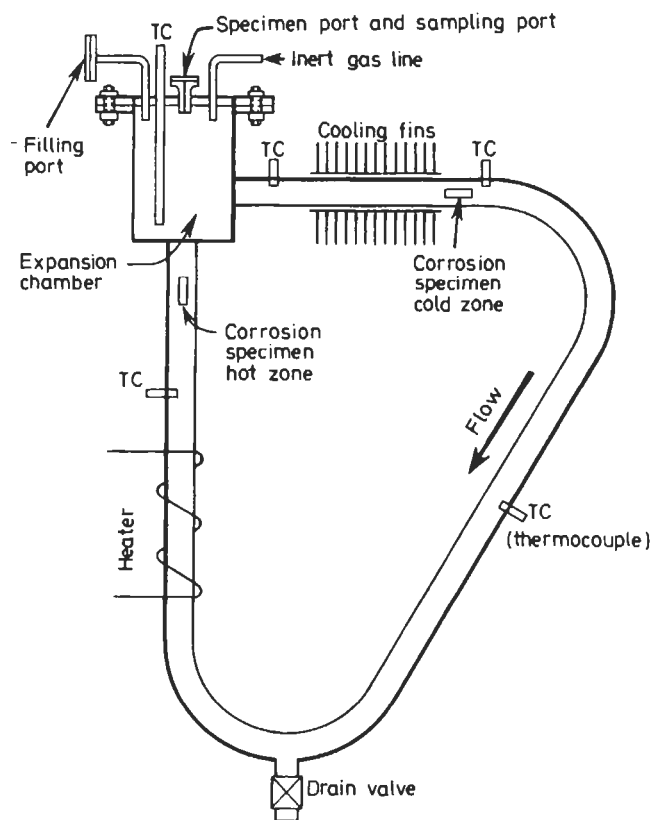


Fig. 19.26 Loop test for studying the corrosion produced by molten metals or salts

heated to the maximum temperature, (b) an economiser or regenerative heat exchanger and (c) a cold leg, where the liquid is cooled to its minimum temperature. The economiser consists of concentric tubes with the hotter liquid flowing through the inner tube whilst the cooler liquid flows in the opposite direction through the annulus between the two tubes, thus minimising power requirements. The material under test may be used for constructing all parts of the loop, and the loop is then destructively examined after a given period of test. However, this is costly and it is now usual practice to use the loop as a permanent testing facility and to test specimens that are generally placed in the hot leg. Assessment of corrosion is based on changes in weight, dimensions, composition, mechanical properties and microstructure.

The final stage in a testing programme is the design, construction and testing of loops that simulate the type of system for which data are required.

Because sodium, which is liquid between about 100°C and 881°C , has excellent properties as a heat-transfer medium, with a viscosity comparable with that of water and superior heat conductivity²⁹⁹, much attention has been paid to liquid sodium corrosion testing of metal and alloys. Indeed, ASTM have issued a Standard Practice which can be used for determination

of the corrosion of ferrous alloys, austenitic stainless steels, high nickel alloys and refractory metals in pumped flowing sodium (ASTM G68:1980). This includes guidance on the monitoring and control of impurity levels in liquid sodium. The oxygen content of the liquid sodium can be measured continuously by an electrochemical oxygen meter³⁰⁰. Similar electrochemical sensors have been used to monitor the carbon content of liquid sodium³⁰¹ and the oxygen content of liquid Li-17Bi eutectic³⁰². The purity of the liquid metal can be maintained by means of a cold trap through which a small part of the flow is continuously bypassed, the purity level being determined by the temperature of the trap. The ASTM Standard Practice gives the following relationship between the cold trap temperature and oxygen content of the liquid sodium:

$$\log_{10} C(\text{ppm oxygen}) = 7.0058 - 2820/T \text{ (K)} \quad \dots (19.18)$$

and recommends that the oxygen level of liquid sodium be lowered to 2.85 ppm or less, corresponding to a cold trap temperature of about 150°C. Borgstedt and Frees²⁷⁹ found that a cold trap operating at 125°C further reduced the oxygen content of liquid sodium to 1–2 ppm and acted as a sink for carbon, reducing the level of this element to about 0.01 ppm. The maintenance of low impurity levels in the liquid metal is facilitated if the inert cover gas in the expansion chamber is of high purity (e.g. ≥99.996% argon).

Evaluation of loop-test results Although the thermal loop test approximates to the conditions which obtain in a dynamic heat-transfer system, in evaluating the results it is necessary to be aware of those aspects in which the test differs from the full-scale unit, as otherwise unwarranted confidence may be placed in the data. Assuming that adequate attention has been paid to the purity and condition of components, etc., the following factors will, according to ASTM G68:1980, influence the observed corrosion behaviour:

1. liquid metal temperature;
2. degree of non-isothermality of the liquid metal system;
3. liquid metal flow rate;
4. heat flux at the corroding surface;
5. surface-area/volume ratio of solid metal/liquid metal;
6. relative sizes of dissimilar metal surface areas exposed to the liquid metal at the various system temperatures.

The relation between corrosion, and maximum temperature and temperature gradient is obvious, since solubility varies as a function of temperature. If the results are to be useful, these factors should match those anticipated in service. Erratic temperature cycling should be avoided as this can also modify the corrosion behaviour. The effect of surface-to-volume ratio will be more pronounced in thermal-convection than in pump loops. It can readily be seen that if a relatively small volume of liquid passes through a given isothermal segment of loop per unit time it will become saturated quickly and the corrosion rate will appear lower than would be the case if a substantially larger volume of liquid were passing at the same velocity. In a pumped loop, the velocity can be maintained sufficiently high to prevent the attaining of equilibrium between the solid and liquid phases, and the

rate of dissolution of the solid will be the controlling step. The flow velocity, or Reynolds number, will affect this step too, in that increased velocity will decrease the stagnant or lamellar layer adjacent to the tube wall and decrease the diffusion path that particles must negotiate to enter the rapidly moving stream²⁸⁸. The turbulence of the flow may also be modified by the manner in which test specimens are inserted in the loop, and this should also be considered carefully in designing a test unit.

The corrosion rates of the materials of construction are always of importance, but it has been found that, whereas the uniform removal of metal from the hot leg may not impair the load-carrying ability of the container, the deposition of metal in the cold leg can cause the cessation of flow, and the measure of the suitability of an alloy is often the time, under given conditions, that it takes for plugging to occur. Again, the flow velocity and the cross-sectional area are of primary importance in relating test results to operating conditions.

The ultimate test, short of constructing a full-scale unit, is to build a small-scale system in which each item to be incorporated in the final device is represented. Such programmes are too specialised to warrant discussion here, and are fully described in the literature³⁰³⁻³⁰⁶.

Liquid-Metal Embrittlement

Metals have sometimes been observed to crack almost instantaneously when wetted by certain molten metals and subjected to plastic strain at temperatures far below those at which the diffusion-ruled processes involved in liquid-metal corrosion attain significance³⁰⁷. The fracture appears to be more brittle than in the absence of the liquid metal, leading to decreased elongation and reduction of area values and, in severe cases, brittle intergranular fracture. Like other forms of environmental cracking, liquid-metal embrittlement is highly specific according to alloy and environment. For example, molten zinc can cause liquid-metal embrittlement of stainless steel if the oxide film is damaged, and because of this molten zinc from associated galvanised parts poses the greatest hazard in welding stainless steel equipment³⁰⁸. Other well known examples of liquid-metal embrittlement include the effects of solder on copper alloys and carbon steels and those of mercury on aluminium and nickel alloys. It is generally accepted that most cases of liquid-metal embrittlement arise from the effects of chemisorption of liquid-metal atoms and the consequent reduction of the tensile strength of interatomic bonds at the crack tip since rates of crack growth (up to 10 cm s^{-1}) are usually rapid compared with rates of diffusion of embrittling atoms ahead of cracks or dissolution of the solid in the liquid metal³⁰⁹. However, there are a few cases where diffusion of embrittling atoms ahead of cracks or selective dissolution of a particular phase of an alloy can produce degradation of materials in liquid-metal environments³¹⁰.

Prerequisites for liquid-metal embrittlement are that a solid metal should be subjected to tensile plastic strain while wetted by a liquid metal in which it has low solubility. It has been suggested that such embrittlement may be a general phenomenon occurring under appropriate conditions and to varying degrees between all solid-metal/liquid-metal couples and that a

single mechanism may be responsible for all liquid metal embrittlement failures³¹¹. The occurrence and severity of the embrittlement are governed by:

1. the particular solid-metal/liquid-metal combination;
2. the temperature;
3. the strain rate;
4. the initial mechanical and metallurgical state of the solid metal.

The most commonly used method for assessing liquid-metal embrittlement is by tensile deformation at a slow strain rate. During testing, the specimen should be immersed in the liquid metal in a sealed autoclave to avoid contamination by atmospheric gases³⁰⁷. Electrochemical probes similar to those employed in liquid metal corrosion testing can be used to monitor the purity of the liquid metal. Susceptibility to liquid-metal embrittlement can be assessed in terms of the uniform elongation, reduction in area and fracture appearance of the specimen relative to that determined under similar testing conditions in an inert environment at the same temperature. Where information on crack-propagation behaviour is required, use can be made of pre-cracked specimens. These can be tested under static or cyclic loading conditions to determine threshold stress intensity factors and crack growth rates³¹².

Tests in Plant

Although laboratory tests (NACE TMO 169-76, and Reference 313) are obviously of value in selecting materials they cannot simulate conditions that occur in practice, and although an initial sorting may be made on the basis of these tests ultimate selection must be based on tests in the plant. This is particularly important where the process streams may contain small concentrations of unknown corrosive species whose influence cannot be assessed by laboratory trials. Testing is also important for monitoring various phenomena such as embrittlement, hydrogen uptake, corrosion rates, etc. which are considered in Section 19.3.

Corrosion Racks

Exposure of coupons or specimens to the process stream cannot be achieved satisfactorily unless they are rigidly supported in a rack, although in some cases it may be possible to simply hang them in by means of a wire. Methods of exposure coupons are described in ASTM Method G4:1984.

In the birdcage rack, disc specimens are mounted on a central rod, and are insulated from each other and from the rod by insulating spacers and an insulating tube, respectively. P.t.f.e. has been found to be suitable for this purpose in aggressive media, particularly at high temperatures. Plates at the end of the rack act as bumpers to prevent the specimens touching the side walls, and the assembly is constructed from a corrosion resistant material such as Monel. Advantages of this method are (1) electrical insulation avoids galvanic effects and (2) the method of holding the specimen at

the centre avoids losses due to corrosion around the point of support. The disadvantages are (1) specimens are not subjected to either heating or cooling effects and thus will not disclose 'hot-wall' effects and may also escape corrosive condensates when the specimens are in a vapour stream above the dew point, and (2) the corrosivity of the environment may be affected by the presence of corrosion products of the construction material of the racks or by corrosion products of adjacent specimens. A further disadvantage is that because of its size and shape it must be inserted into the process stream when the plant is out of service. Special devices are required for mounting specimens within pipelines so that they will be subjected to velocity effects.

The *insert rack* is designed for easy installation and removal through an unused nozzle. The supporting rods (one for each specimen) are welded to a single support plate that is of a width that enables it to be introduced through the nozzle. However, this too cannot be inserted unless the equipment is out of service, although its introduction does not require removal of gas.

A slip-in rack is described by Dillon, *et al.*³¹⁴ (Fig. 19.27) that is designed to be inserted and removed during the operation of the plant through a full-port gate valve attached to a nozzle of suitable diameter (3.8–5.1 cm). It consists of a short length of pipe flanged at one end to match the gate valve and having a backing-gland arrangement at the other. The coupons are mounted on a rod of small diameter welded to a long heavier rod. The valve is opened and the support rod is pushed through the packing gland so that the specimen is introduced into the process stream. The specimens are removed by withdrawing the rod until they are again within the pipe section, the gate valve is closed and the rack removed from the valve.

Access fittings are available (e.g. Cosasco* access fitting) that enable specimens to be introduced into plant that is operating at high pressures, but can also be used for ambient pressures (see Section 19.3). In some instances it is possible to secure valuable information by substituting experimental materials for parts of the operating equipment, a practice that is used most frequently with condenser tubes, evaporators or other heat exchangers or sections of piping systems.

The prediction of materials performance in plant conditions using modelling and corrosion test methods has been discussed by Strutt and Nichols³¹⁵.

Specimens

A convenient size for a circular coupon is 3.8 cm dia., a thickness of 0.32 cm and a central hole of 1.1 cm. Although inherent in the philosophy of corrosion testing, the use of coupons with surfaces that simulate those in service has been found to be unsatisfactory owing to irreproducibility, and the standard procedure normally adopted is to abrade down to 120-grit. ASTM Method G4:1984 gives details of preparation of specimens, evaluation of replicate exposures and the application of statistical methods.

*Grant Oil Tool Company.

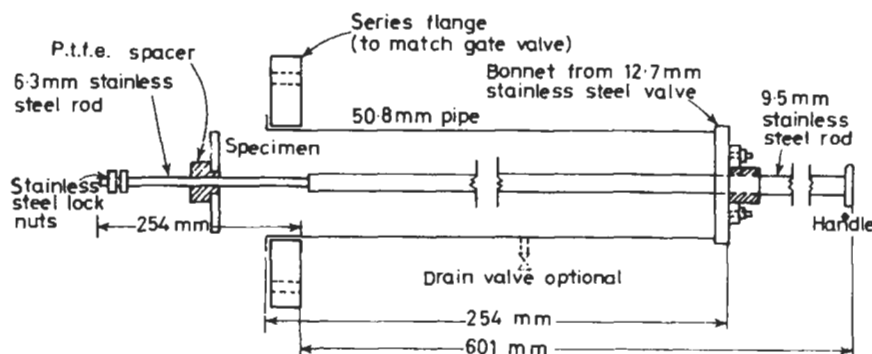


Fig. 19.27 Slip-in corrosion test rack (after Dillon *et al.*³¹⁴)

Atmospheric Tests

More or less standardised techniques have been developed for the exposure of specimens to atmospheric weathering. ASTM G50:1976 (R1984) and ISO 8565:1992 provide guidance on conducting atmospheric corrosion tests on metals, alloys and metallic coatings. Procedures for recording data from atmospheric corrosion tests on metallic-coated steel specimens are given in ASTM G33:1988. The usual practice in the USA³¹⁶ is to mount bare specimens on racks that slope 30° from the horizontal and painted specimens on racks that slope 45° from the horizontal. The usual orientation is to have the specimens face south. In coastal exposures it is not uncommon to have the specimens face the ocean. Steel specimens exposed vertically have been found to corrode about 25% more than similar specimens exposed at the 30° angle³¹⁷. Vertical exposure was used in the large-scale tests of non-ferrous metals undertaken by Subcommittee VI of ASTM Committee B-3³¹⁸. Vertical exposure is also favoured by Hudson³¹⁹.

A typical test installation uses a frame to support racks on which the specimens are mounted by means of porcelain or plastics insulators. The insulators may be spaced to take specimens varying in size from 10.1 × 13.4 cm to 10.1 × 32 cm and even larger specimens may be used for certain tests. Special types of exposure have been devised to take into account important effects of partial shelter and accumulation of pools of water, as in the case of the specimen and method of support used by Pilling and Wesley³²⁰ to compare steels for roofing.

Copson³²¹ has described in considerable detail the several factors that require attention in studying atmospheric corrosion, particularly of steels.

Several sizes and shapes of specimens have been used in addition to the common ones already mentioned. In the long-time test of bare and zinc-coated steels undertaken by ASTM Committee A-5 on Corrosion of Iron and Steel, full-size sheets were used³²². This Committee has also exposed specimens in the form of hardware³²³ and wire and fencing³²⁴.

The extent of deterioration may be measured by one or more of the following methods: visual examination, change in weight, change in tensile properties. Visual inspection was depended upon primarily in the A-5 tests

of steel sheets³²⁴. Here, visible perforation more than 6 mm from an edge was the criterion of failure. This leaves much to be desired for close comparisons because of the frequency with which perforations may be obscured by heavy coats of rust³¹⁷. Other shortcomings of the use of time to visible perforation as the criterion of corrosion resistance are as follows.

1. The removal of rust films or other corrosion products to facilitate inspection for perforation prior to termination of the exposure will change the natural performance of the material, and is therefore not tolerable.
2. The recording of a perforation establishes only the time to failure and provides no idea of the progress of corrosion up to the point of failure.
3. The time to perforation may be influenced considerably by the random occurrence of pits that happen to meet after starting from opposite sides of a sheet. This chance meeting of pits may be determined only to a slight extent by the composition of the material and, therefore, will interfere with observations of the effects of composition.

Where changes in appearance are of paramount interest, as in the case of metallic and organic coatings on steel or other metals, visual examination is most desirable. To facilitate ratings on such a basis, photographic standards have been employed, as, for example, in tests on chromium-plated steel undertaken by ASTM Committee B-8 on Electrodeposited Metallic Coatings³²⁵. These ratings are supplemented by a shorthand description of the nature of the deterioration observed.

Similarly, photographic standards are recommended for rating organic coatings with respect to different modes of deterioration in ASTM D610:1985.

The most precise measurements of corrosion resistance require the use of specimens that can be weighed accurately after careful removal of corrosion products by the techniques described earlier.

A sufficient number of specimens should be exposed initially to permit their withdrawal from test in appropriate groups, for example 3 to 5 duplicates after at least three time intervals. For long-time tests, a suitable schedule would call for removals after 1, 2, 5, 10 and 20 years.

It is good practice to determine depths of pitting as well as mass loss.

As is the case with other types of corrosion testing, mass-loss determinations may fail to indicate the actual damage suffered by specimens that are attacked intergranularly or in such a manner as dezincification. In such cases, mechanical tests will be required as discussed already in the section on evaluation techniques.

It is desirable for reporting of atmospheric corrosion tests to include a precise description of the climatic conditions that prevailed at the test site during the test so that the weather factors can be tied in with the results of exposure. Progress towards this aim has been made recently with the development of international standards which provide guidance on evaluating the corrosivity of atmospheric environments. Atmospheric corrosivity can be expressed in terms of environmental factors, the most important of which have to do with contaminants of the atmosphere and the time that the specimens are actually wetted by condensed moisture. In the case of organic coatings, the interacting effects of sunlight and moisture, and their

sequence, complicate this problem even more³²⁶. Methods of measuring pollution (deposition rates of sulphur compounds and chlorides) are provided in ISO/DIS 9225:1989. ISO/DIS 9223:1989 defines five different categories of atmospheric corrosivity based on time of wetness and pollution. An alternative approach is to express atmospheric corrosivity in terms of the corrosion rate of standard materials, including carbon steel, weathering steel, zinc, copper and brass. Methods of determining the corrosion rates for this purpose are given in ISO/DIS 9226:1989, while ISO/DIS 9224:1989 provides a classification of atmospheric corrosivity based on both the average and the steady-state corrosion rates of the standard metals.

Sereda³²⁷ has described a method of determining time of wetness in which a strip of platinum foil (0.8×7 cm) is mounted on a zinc panel (10.1×13.4 cm) on both the skyward and groundward face. Condensed moisture from dew, or rain or snow, results in a galvanic cell whose potential is monitored on a recorder, thus giving the time of wetness. Guttman and Sereda³²⁸ found that if the SO_2 content remained essentially constant the corrosion rate of zinc was related to time of wetness; furthermore, the dew detector registered the presence of moisture on the panel when the relative humidity ranged between 82 and 89%, thus providing a means of estimating from long-term weather data, such as temperature and relative humidity, the time a specimen is likely to be wet.

Atmospheric Galvanic Tests

Studies of galvanic corrosion in the atmosphere are experimentally simpler than those conducted in solution in the laboratory. The environment is taken as it comes and the relatively high electrical resistance of the rain and moisture films that serve as electrolytes restricts the distance through which the galvanic action can extend, and thus limits the relative area effects that complicate galvanic corrosion in solutions of high conductivity. Standard test methods for assessing galvanic corrosion caused by the atmosphere are given in ASTM G104:1989 and in ISO 7441:1984 (see also Section 1.7).

Because of the limited proportion of the areas of a couple that actually participates in the galvanic action, it is difficult to make quantitative measurements that separate the galvanic action from the total effects of exposure. Thus many of the observations are likely to be qualitative ones, and often no more than what can be determined by visual inspection or measurements of changes in strength, etc. as a result of any localised galvanic action.

An idea of the distribution of galvanic corrosion in the atmosphere is provided by the location of the corrosion of magnesium exposed in intimate contact with steel in the assembly shown in Fig. 19.28 after exposure in the salt atmosphere 25 m from the ocean at Kure Beach, North Carolina, for 9 years. Except where ledges or crevices may serve to trap unusual amounts of electrolyte, it may be assumed that, even with the most incompatible metals, simple galvanic effects will not extend more than about 4–5 mm from the line of contact of the metals in the couple.

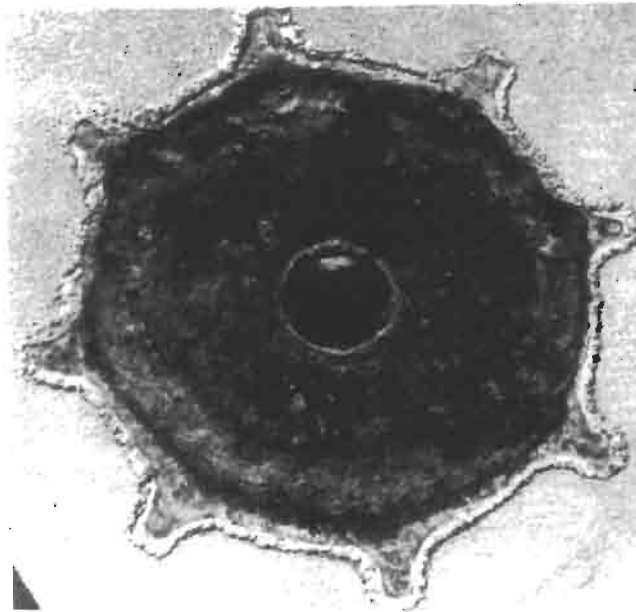


Fig. 19.28 Distribution of galvanic effects around contact of a magnesium casting and a steel core

The extent of galvanic action in atmospheric exposure may also be restricted by the development of corrosion products of high electrical resistance between the contacting surfaces — this is especially likely to occur if one of the metals in the couple is an iron or steel that will rust. In long-time tests such possible interruptions in the galvanic circuit should be checked by resistance measurements from time to time so as to determine the actual periods in which galvanic effects could operate.

The test assembly used originally by Subcommittee VIII of ASTM Committee B-3 in its comprehensive studies of atmospheric galvanic corrosion³²⁹ had the disadvantage that it depended on paint coatings to confine corrosion to the surfaces in actual contact with each other. In interpreting the results, it was frequently difficult to decide how much corrosion was due to galvanic action and how much to a variable amount of normal corrosion through failure of the paint system.

These difficulties were overcome in a design developed by Subcommittee VIII of ASTM Committee B-3³³⁰ (Fig. 19.29). In this assembly each of the two middle specimens has a specimen of the other metal each side of it and only these middle specimens are considered in appraising the results.

A fairly direct way of observing galvanic effects, which also permits changes in mechanical properties to be measured, involves the preparation of a composite specimen formed by attaching a strip, or strips, of one metal to a panel of another one. Tensile test specimens that include the areas of galvanic action can be cut from these panels after exposure, as shown in Fig. 19.30.

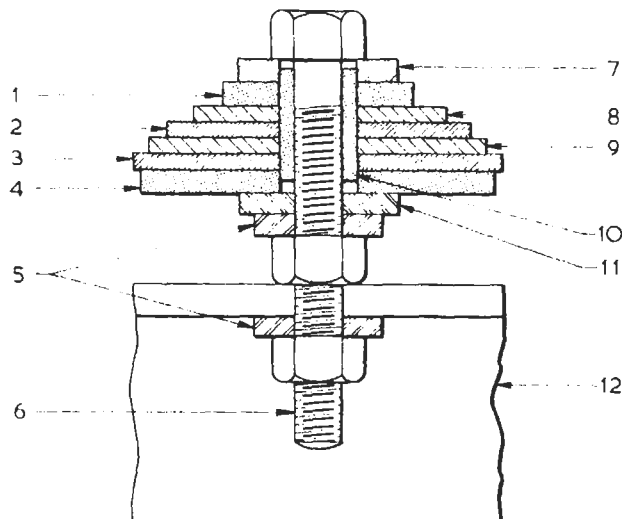


Fig. 19.29 Atmospheric galvanic couple test assembly

KEY

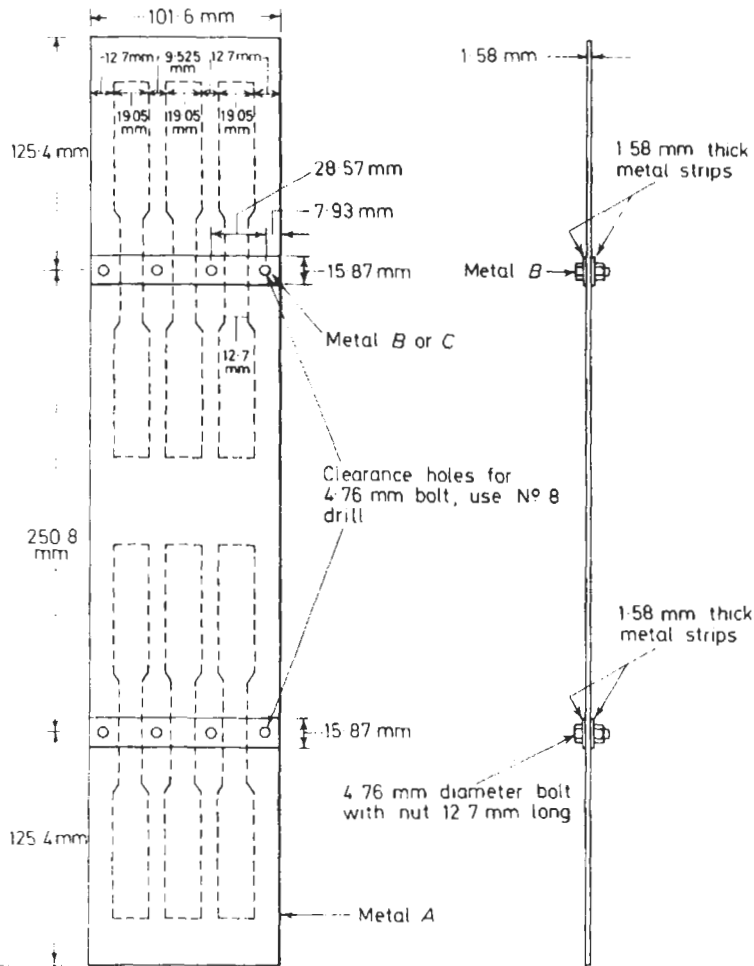
- (1) Bakelite washer 19.0 × 3.2 mm. (2) Metal *B* disc 30 × 1.6 mm. (3) Metal *B* disc 36.6 × 1.6 mm. (4) Bakelite washer 35.5 × 3.2 mm. (5) Stainless steel lock washer. (6) Stainless steel bolt 4.8 × 38.1 mm. (7) Stainless steel washer 15.9 mm o.d. (8) Metal *A* disc 25.4 × 1.6 mm. (9) Metal *A* disc 35.5 × 1.6 mm. (10) 11.1 mm Bakelite bushing, 5.2 mm i.d. × 7.9 mm o.d. (11) Stainless steel washer 15.9 mm o.d. (12) Galvanised angle support

A modification of the specimen shown in Fig. 19.30 may be made simply by lapping a panel of one material over a panel of another one. The greatest effects may be observed when such panels are exposed with the laps facing up so as to favour retention of corrosive liquids along the line of contact. To permit observations of secondary effects of corrosion products, or exhaustion of corrosive constituents, the relative positions of the dissimilar metals should be changed from top to bottom in duplicate test assemblies.

Where the practical interest is in possible galvanic effects of fastenings, it is simple to make up specimens to include such couple assemblies as illustrated in Fig. 19.31.

A type of assembly calculated to favour maximum galvanic action was developed by the Bell Telephone Laboratories and is illustrated in Fig. 19.32. Here, the less noble metal is in the form of a wire wound in the grooves of a threaded specimen of the metal believed to be more noble. Good electrical contact is achieved by means of set screws covered with a protective coating. This assembly favours accumulation of corrosive liquids around the wire in the thread grooves. Corrosive damage is also favoured by the high ratio of surface to mass in the wire specimens.

To determine whether a protective metallic coating will retard or accelerate corrosion of a basis metal, and to what distance either effect will extend, specimens in which strips of various widths are left bare or made bare have been used by Subcommittee 11 of ASTM Committee B-8³³⁰. The extent of corrosion in and near the bare strips as compared with that on a



completely bare or completely coated specimen will provide a measure of the extent of galvanic action and the distance through which the effect is able to extend from the edges of the bare strips.

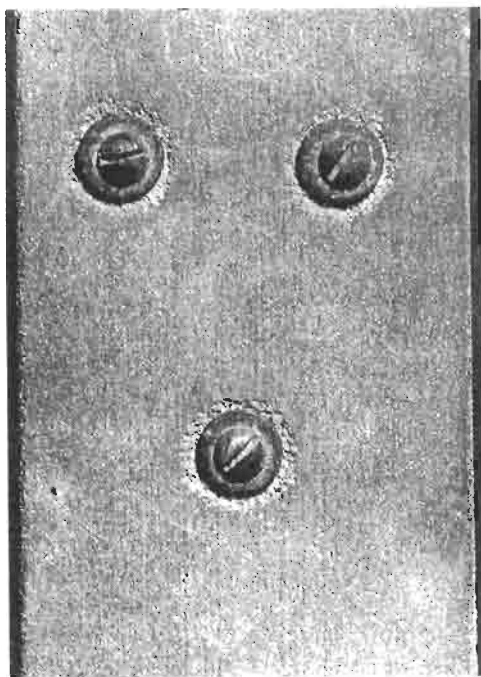


Fig. 19.31 Specimen for studying galvanic corrosion resulting from fasteners

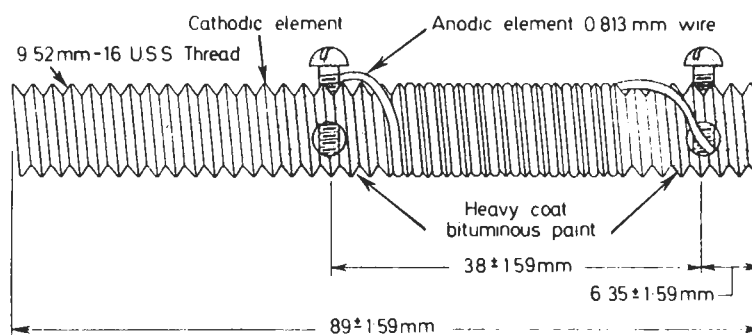


Fig. 19.32 Bolt and wire type atmospheric galvanic couple test specimen

form of wires, plates, tubes, etc., and certain general precautions should be followed.

1. The specimens should be mounted so that they are insulated from their supporting racks and from each other. Such insulation can be achieved by the use of fastening assemblies, such as illustrated in Fig. 19.33. Occasional difficulties have been encountered with this sort of assembly for tests of copper and high-copper alloys because of deposition of copper from corrosion products along the surfaces of the insulating tubes which provided a

metallic bridge between the specimens and the rack and introduced undesired galvanic effects. The required insulation and support can be provided by use of porcelain or plastics knob insulators in much the same manner as used on atmospheric test racks. A modified design has the advantage of offering less resistance to the flow of water and is less likely to serve as a form of screen to catch débris floating on, or suspended in, the water. Additional details of rack design may be found in the section on sea-water tests in *The Corrosion Handbook* (Uhlig, Selective Bibliography).

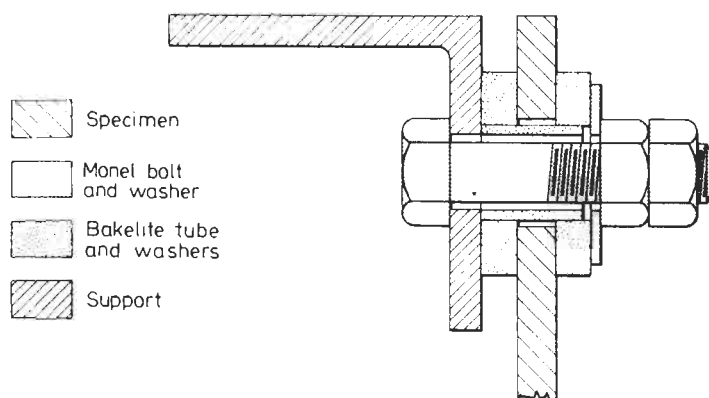


Fig. 19.33 Scheme for insulating specimens from metal test racks

2. In the case of corrosion tests in the sea or in other large volumes of water, i.e. as opposed to tests in waters flowing within pipes, all the specimens to be compared should be suspended at the same depth or should pass through the same range of depths. Isolated specimens exposed at different depths will not be corroded in the same way as continuous specimens that extend through the total range of depth to be studied. This is especially the case with specimens exposed to sea-water from above high tide to below low tide. Where the behaviour of structures, such as piling, that pass through these zones is to be investigated, the test specimens must be continuous and large enough to extend through the total range in order to take into account differential aeration and other possible concentration cells that may have such a tremendous effect on the results secured³³¹. For example, in sea-water exposure, isolated specimens of steel exposed in the tidal zone have corroded 10 times as fast as portions of continuous specimens of the same steel in the same zone that extended also below low-tide level³¹⁷.

3. The specimens should be oriented so that their flat surfaces are parallel to the direction of water flow and so that one specimen will neither shield an adjacent specimen from effects of water velocity nor create any considerable extra turbulence upstream of it.

4. In tests in sea-water where accumulations of marine organisms are likely, specimens exposed parallel to each other should be spaced far enough apart to ensure that the space between specimens will not become completely

clogged by fouling organisms. A minimum spacing of 100 mm is suggested.

5. Wooden racks used in sea-water tests are likely to be subject to severe damage by marine borers. The wood used, therefore, must be treated with an effective preservative, for example creosote applied under pressure, if the test is to extend for several years. Organic copper compound preservatives may suffice for shorter tests, for example 2 or 3 years. Since the leaching of such preservatives may have some effects on corrosion, metal racks fitted with porcelain or plastics insulators have an advantage over wooden racks.

6. Where constant depth of immersion is desired in spite of tidal action, it is necessary to support the test racks from a float or raft.

Recommended methods for assessing the corrosivity of waters, including flowing potable waters, are described in ASTM D2688:1983. Three procedures are described in which test specimens in the form of wires, sheets or tubes are placed in pipes, tanks or other equipment. The test assembly for the first of these consists of three helical wire coils mounted in series on, and electrically insulated from, a supporting frame. The assembly must be installed so that flow is not disturbed and turbulence and high velocities, e.g. of more than 1.53 ms^{-1} , are avoided. A minimum test period of 30 days is recommended. Procedures for the other specimen forms are given in the standard.

An extensive study of the corrosion of metals in tropical environments has been carried out by Southwell, *et al.*³³². Tests have included atmospheric exposure, and exposure in sea-water under mean tide and fully immersed conditions for a range of ferrous and non-ferrous metals and alloys.

The Marine Corrosion Working Party of the European Federation of Corrosion has published valuable advice on corrosion testing in service³³³.

Field Tests in Soil

The precautions generally applicable to the preparation, exposure, cleaning and assessment of metal test specimens in tests in other environments will also apply in the case of field tests in the soil, but there will be additional precautions because of the nature of this environment. Whereas in the case of aqueous, particularly sea-water, and atmospheric environments the physical and chemical characteristics will be reasonably constant over distances covering individual test sites, this will not necessarily be the case in soils, which will almost inevitably be of a less homogeneous nature. The principal factors responsible for the corrosive nature of soils are the presence of bacteria, the chemistry (pH and salt content), the redox potential, electrical resistance, stray currents and the formation of concentration cells. Several of these factors are interrelated.

These considerations will significantly affect the location of test specimens in field testing. It is clearly important to ensure that the conditions of exposure are accurately known so that the corrosion test results may be interpreted with respect to the end-use requirements.

Two civil engineering operations require particular attention when soil corrosion tests in the field are required. These are (1) the use of reinforced earth structures in which the corrosion conditions will differ from those at

the site from which the soil has been taken and which may take some time to come to equilibrium in the new site, and (2) the use of reclaimed or contaminated land where unusual corrosive agents may be present in irregular distribution. In both these situations considerable thought should be given to the corrosion test procedures.

Soil burial tests are popular despite the precautions that are needed. It is also important that a sufficient number of specimens are exposed so that statistical treatment of the results may be applied to compensate for some of the inevitable variations in the exposure conditions. Certain precautions originally set out in 1937³³⁴ are still valid, and are as follows:

1. A sufficient number of specimens to yield a reliable coverage should be included.
2. The test site should be typical of the type of soil to be investigated.
3. The depth of burial should be that which will be occupied by the structure of interest. Specimens to be compared should be buried at the same depth. Ideally, tests for structures, such as piling, that will extend through several horizons would require the use of test specimens long enough to extend to the same depth.
4. Specimens should be separate so that they will not affect the corrosion of each other. A minimum spacing of two diameters was proposed.
5. Cylindrical specimens should be laid horizontally.
6. Sheet or plate specimens should be placed on edge.
7. The ends of pipe specimens should be closed to prevent internal corrosion.
8. Sufficient specimens should be provided to allow withdrawals after several time intervals so as to permit observations of changes in corrosion rates with time.
9. A portion of the original surface should be protected so as to provide a datum line for the measurement of pit depths.
10. In applying results of tests on small specimens to estimating corrosion, particularly by pitting on large structures, the effect of the increased area in increasing the depth of pitting must be taken into account³³⁵.

Other Tests

Other tests to determine bacterial—notably sulphate reducing—activity, soil resistivity, pH, redox potential, etc., will provide valuable data to supplement the results obtained with test specimens. A useful account of some of these was given in Reference 336 and they are also discussed in Sections 2.6 and 10.7. A scheme for assessment of corrosivity of soils based on some of the above parameters has been given by Tiller³³⁷.

A number of standards exist for the determination of some of these parameters. BS 1377:Part 3:1990 refers to methods of tests for soils for civil engineering purposes, and Part 9 refers to these and corrosivity tests *in situ*. It is significant that the standard draws attention to the fact that the results of the tests that are described should be interpreted by a specialist. ASTM tests for pH and resistivity of soil used for corrosion testing are covered by G51:1977(R1984) and G57:1978:(R1984), respectively.

Corrosion Testing of Organic Coatings

Programmes to evaluate the corrosion protection by organic coatings on metals are intended to establish relationships between coating properties and performance. Such knowledge is essential to the most effective use of organic coating systems in corrosion control. Depending on the detail with which such studies are performed, light may be shed on the mechanism of coating deterioration as well.

If valid and useful relationships are to be established, it is essential that the factors affecting performance be recognised and form part of the test record. Since the performance is determined by interactions between the coating, the substrate and the surrounding environment against which protection is sought, significant factors and their interrelationships will vary with the nature of the service.

Care in designing and conducting the test in no way reduces the need for discrimination on the part of the person using the test data in the selection of a coating for a particular purpose. Test environments must reflect the deteriorating influences of the service for which they are applicable. A coating system cannot reliably be selected for service in a chemical plant on the basis of performance determined in a rural atmosphere.

Thus, both the proper conduct of the testing programme and the valid use of the data depend on an understanding of the nature of organic coatings and of the forces through which they are degraded.

Behaviour of Organic Coatings

An organic coating provides corrosion protection through the interposition of a continuous, adherent, high-resistance film between the metal surface and its environment (see Section 14.3). In principle, its function is the mechanical exclusion of the environment from the metal surface. It seldom, if ever, succeeds practically in achieving this since all continuous organic films are permeable to some degree to moisture and many coatings either have occasional physical defects or acquire them in service. Surface conversion treatments, such as phosphate and chromate dips, are used to supplement the physical protective properties of coatings, as are chemically inhibiting primers and wash primers. When such treatments are used, they must be included in the record as constituting a part of the coating system.

Paints are considered in detail in Chapter 14, paint failures being discussed in Section 14.4.

Critical parts of the test programme are the preparation of test specimens, the selection of the exposure conditions (both in laboratory and field tests) and the selection of significant coating properties to be evaluated as a measure of deterioration with time.

Preparation

Specimens will normally be flat panels, large enough to avoid any effects caused by nearby edges of the specimen. Edges and backs are usually coated

unless the effect of uncoated edges is an intended test variable. Panels may include the structural features of plates, channels, welds, sharp edges, pits or depressions, depending on the service for which the data are to be applicable.

The composition of the basis metal has been found to influence the performance of organic finishes in many cases. Thus, composition is a significant test variable and must be considered in comparing test data.

It is particularly important that surface roughness and cleanness, which greatly affect adhesion, should be carefully controlled and that the procedures used to achieve them be a part of the test record. A high degree of cleanliness is normally sought. If, however, the data are to be applicable to the painting of outdoor structures, a certain amount of outdoor weathering becomes a part of the specimen preparation prior to coating. Specimens again will be of the basis metal appropriate for the related service application.

The thickness of a coating plays an important part in determining its physical characteristics. Uniformity of thickness among specimens therefore is necessary, particularly when coating deterioration is to be assessed by changes in such properties. For the preparation of reproducible specimens, methods of applying coatings in uniform thicknesses are available, as are methods for accurately measuring film thickness.

Exposure Conditions

In considering exposure tests, whether in the form of laboratory, field or service tests it is important to consider the purpose of the test and the relevance of the data to the anti-corrosion function of the coating. Thus, in the case of paint coatings, factors such as gloss deterioration, chalking and colour retention are of considerable importance in some industries, for example the automotive industry, but perhaps of minor importance in the painting of structural steelwork. These assessment factors can nevertheless be of significance since they may be the precursors of corrosion of the basis metal.

Laboratory tests Laboratory tests are often conducted with the purpose of providing an accelerated test procedure and if intelligently used, i.e. with proper respect for their limitations, are of value in determining the probable order of durability and hence, by implication, corrosion protection of a group of paints. They can also be of value in assessing the quality of a range of similar compositions where there is already some knowledge of the performance of the general composition. Although continuing attention is given to the correlation of accelerated tests with field trials and service performance, caution must always be exercised in attempting to predict the type of failure likely to occur under conditions of natural exposure. Certainly an approach based on 'the rougher the treatment the better the test' cannot be justified. Three main classes of laboratory test can be identified and may be conveniently classified under the headings of (1) electrochemical (2) coating adherence and (3) exposure cabinets—including weatherometers.

Electrochemical tests This group includes the various electrochemical tests that have been proposed and used over the last fifty or so years. These tests include a number of techniques ranging from the measurement of potential-time curves, electrical resistance and capacitance to the more complex a.c. impedance methods. The various methods have been reviewed by Walter³³⁸. As the complexity of the technique increases, i.e. in the above order, the data that are produced will provide more types of information for the metal-paint system. Thus, the impedance techniques can provide information on the water uptake, barrier action, damaged area and delamination of the coating as well as the corrosion rate and corroded area of the metal. However, it must be emphasised that the more comprehensive the technique the greater the difficulties that will arise in interpretation and in reproducibility. In fact, there is a school of thought that holds that d.c. methods are as reliable as a.c. methods.

Adherence tests This group of techniques involves the testing of the metal-to-paint adherence. These techniques are covered by descriptions such as prohesion³³⁹, blister³⁴⁰, pull off (BS 3900:Part E10:1979(1989)) and cross-cut (BS 3900:Part E6:1976(1989)). Detailed descriptions of these techniques will be found in the appropriate references.

Exposure cabinets This group of laboratory tests include the so-called exposure cabinets, salt spray and weatherometer tests in which the paint-coated panels are subjected to various cycles of wetting and exposure to ultra-violet light to simulate atmospheric conditions of exposure. BS 3900:Part F3:1971 (1986) describes a weatherometer consisting of a 1.2 m dia. drum that rotates at 1 rev/20 min, and has facilities for spraying the panels (100 × 150 mm) periodically during a 24 h cycle and exposing them to ultra-violet light by means of an enclosed carbon arc. Spraying with distilled water is effected by means of an atomiser and fan using the following 24 h cycle: 4 h off, 2 h on, 10 h off, 2 h on and 1 h off; the final 1 h is used for checking the arc. The test is continued for 7 days at the end of which the panels are examined visually for change of colour, loss of gloss and blistering, and for checking, cracking and chalking by means of a lens (× 25).

An appraisal of artificial weathering methods was given in a report by Hoey and Hipwood³⁴¹ who described the effectiveness of various weatherometer tests such as are described in BS 3900:Part F3 and ASTM E42:1964 (now ASTM G23:1989). Although these tests simulate atmospheric exposure it is not possible to obtain a direct correlation owing to variation in outdoor exposure conditions from place to place, but they serve a very useful purpose in providing a preliminary sorting of paints that can then be tested in the field.

Field and Plant Tests Field exposure of test panels offers the benefit of a high degree of control over surface preparation and application. Moreover, through standardised exposure conditions, broader comparisons between both paint systems and locations are possible. More importantly, since replicates may be removed and laboratory tested periodically, changes in properties can be followed in considerable detail. At least four replicates should be examined for each exposure period to minimise the effects of atypical specimens.

The exposure site is selected according to the service for which the data are to be applicable. For atmospheric service, such factors as marine and industrial contaminants, sunlight, dew and sand abrasion, must be considered. Atmospheric specimens are normally mounted at 45°, facing south. This has been shown to provide about a 2:1 acceleration of failure compared with a vertical exposure. Whether this or other standardised positions are used, the details of the exposure are an important part of the test record.

The degree of deterioration experienced over a given test period varies with climatic conditions. Since these differ significantly from one season to another, a standard specimen, the performance of which is well known, should be included with each exposure to increase the validity of coating comparisons.

For other environments, such as in sea-water or in chemical plants, exposure conditions that most nearly duplicate those of the related service and are at the same time reproducible, are used. Impingement by water or water carrying entrained solids, thermal effects and physical abuse are among the factors to be considered.

Coating Evaluation

The performance of organic finishes on test is evaluated by visual observation and by physical tests made upon coated specimens that have been exposed for various periods of time to natural or accelerated weathering conditions. Electrical tests are sometimes used on immersed specimens.

Inspection of test panels at the test sites consists of visual observations of blistering (*see* ASTM D714:1987) and the appearance of rust (*see* ASTM D610:1985). For these, photographs showing various degrees of degradation which serve as observational standards greatly reduce variations between observers. Results of consecutive observations entered on charts provide visual records of the trend of these features with time.

These more serious evidences of degradation, however, are preceded by invisible physical alterations within the coatings which can be detected readily and quantitatively by suitable physical tests of replicate specimens removed from tests at periodic intervals. The use of such tests to reveal incipient coating changes is, in a sense, a means of accelerating the test programme without distortion of the test environment. This approach is especially dependent on uniformity of properties among replicates, hence on reproducible application techniques. Moreover, since many coating properties are highly sensitive to changes in temperature and relative humidity, equilibrium of the specimens during testing is necessary. Testing conditions are commonly 25°C and 50% r.h.

Physical tests appropriate for this type of evaluation are not necessarily limited to those properties which the coating may be called upon to display in service. A coating that shows a decrease in distensibility from 20 to 10% is still quite capable of withstanding the expansion and contraction of the substrate in atmospheric temperature cycling, yet such a coating can be expected to fail in service earlier than one which shows no decrease. Thus,

the properties of value are those that have been established as reliable indices of deterioration.

Besides providing early comparative data on coating performance, physical tests in dealing with intrinsic coating properties provide much-needed quantitative information on the relationships between the several factors affecting the ageing of organic films. The tests cited below are those which have been shown to indicate reliably significant changes in the condition of coatings on tests.

Distensibility This property is very sensitive to chemical changes within the coating. Its measurement thus shows the beginning of normal ageing or of deterioration through reaction with the environment. Distensibility is generally determined by bending the test panels over a conical mandrel of known radius and calculating the % elongation at first rupture.

Abrasion tests In these tests the end point is normally taken as the amount of abrasion required to penetrate the coating. The results thus reflect the strength of the coating, its cohesion, and in some cases its adhesion to the basis metal as well as resistance to abrasion.

Hardness Coating hardness is related to the method of measurement. Results reflect the resistance to scratching as well as to indentation.

Impact tests Such tests reveal the resistance of coatings to deformation and destruction by concentrated sudden stresses. They thus throw considerable light on the integrity of the metal-coating bond. Changes in adhesion through chemical reaction at the paint/metal interface will be reflected in the impact-test values.

The above tests for characterising coating properties necessarily continue to involve a certain amount of empiricism. The intelligent use of these tests, however, has shown that wide variations of physical and electrochemical characteristics of coatings as a function of composition may be obtained, and further, that significant changes in these characteristics, that can be measured before the usual evidence of failure appears, occur upon natural and accelerated ageing.

Test Methods for Corrosion Inhibitors

Immersed conditions

Since corrosion inhibitors are used in a wide range of applications, no universal test method exists. Recognised methods tend to relate to a product or process in which the inhibitor forms a part rather than to the inhibitor per se. Thus, tests exist for inhibited coolants, cooling waters, cutting oils, pickling liquids, etc.

The considerations applicable to corrosion test methods also apply to tests for inhibited products. The metals and alloys used, their surface preparation, the temperature, flow rate, composition of the test medium, the presence of heat transfer, and so on, must all be relevant to the proposed use of the inhibited product. As with other test methods there are those tests

that have been developed in particular laboratories for the development of inhibitors for particular purposes and those that have acquired national or international recognition by appropriate standards-writing bodies.

The three types of test procedure discussed in this chapter may often be identified in testing of inhibitors or inhibited products. The testing of inhibited engine coolants provides a suitable example.

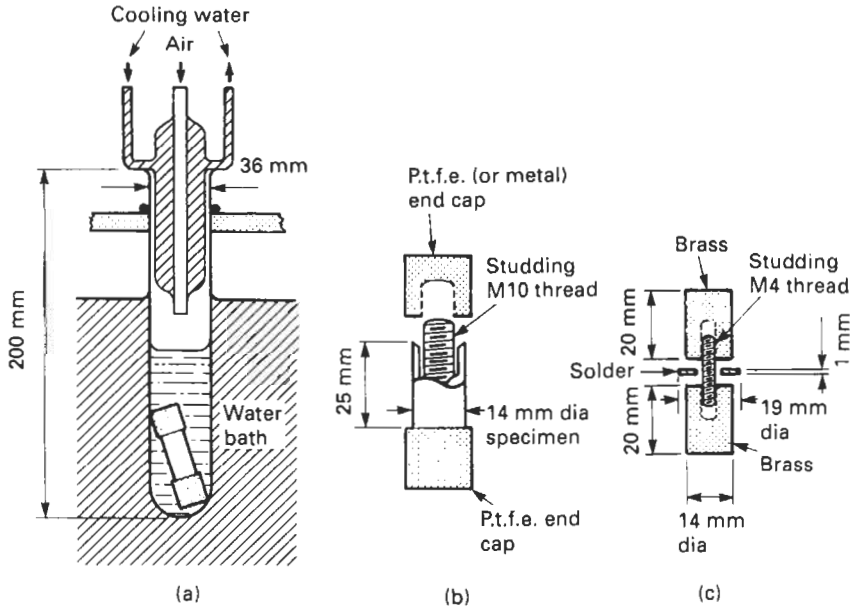


Fig. 19.34 Experimental arrangement for corrosion tests without heat transfer. (a) Test vessel and specimen, (b) specimen assembly for single metal or bimetal specimens, and (c) assembly for brass/solder/brass specimens

Laboratory tests used in the development of inhibitors can be of various types and are often associated with a particular laboratory. Thus, in one case simple test specimens, either alone or as bimetallic couples, are immersed in inhibited solutions in a relatively simple apparatus, as illustrated in Fig. 19.34. Sometimes the test may involve heat transfer, and a simple test arrangement is shown in Fig. 19.35. Tests of these types have been described in the literature^{342,343}. However, national standards also exist for this type of test approach. BSI and ASTM documents describe laboratory test procedures and in some cases provide recommended pass or fail criteria (BS 5117:Part 2:Section 2.2:1985; BS 6580:1985; ASTM D1384:1987). Laboratory testing may involve a recirculating rig test in which the intention is to assess the performance of an inhibited coolant in the simulated flow conditions of an engine cooling system. Although test procedures have been developed (BS 5177:Part 2:Section 2.3:1985; ASTM D2570:1985), problems of reproducibility and repeatability exist, and it is difficult to quote numerical pass or fail criteria.

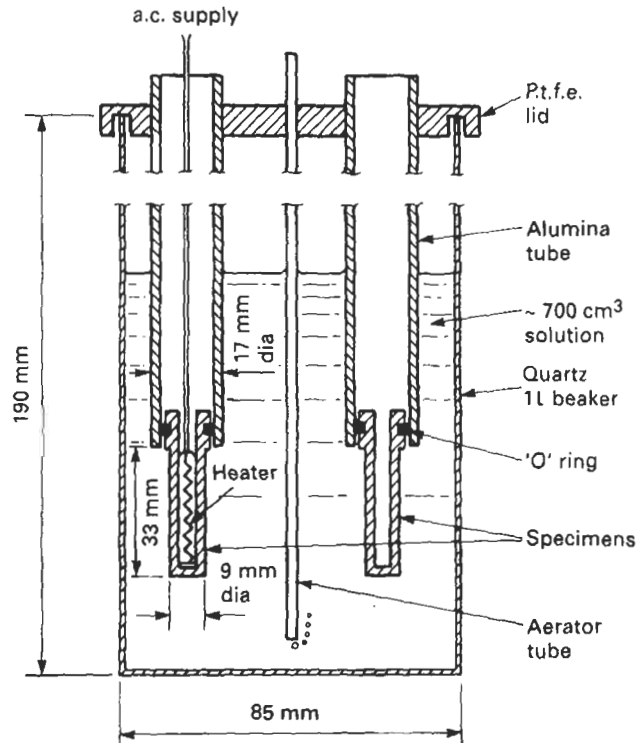


Fig. 19.35 Apparatus for testing inhibitors with metal-to-coolant heat transfer

These laboratory tests may be followed by engine dynamometer tests (BS5117:Section 2.4:1985(1989)) and finally by road tests in working vehicles (BS 5117:Part 2:Section 2.5:1985 (1989)), thus completing the sequence of laboratory, field, service testing.

The problems that have been experienced in the recirculating rig test are indicative of those often met in performance testing. Attempts to reproduce the service conditions in a laboratory test inevitably involve attempting to reproduce each of the controlling conditions that exist in the real situation. Variations, which may be relatively small, in these simulations can lead to significant differences in test results. There is therefore much to be said for keeping test conditions as simple as possible rather than attempting to reproduce accurately the conditions in practice. A balance between reproducibility and realism has to be struck.

An example of a relatively simple, but effective, test method is that developed for inhibited mineral oils in the presence of water (BS 2000:Part 135:1983). Typically, in these tests, a mixture of the inhibited oil and distilled water or sea-water in specified proportions is stirred at 60°C in a beaker containing a steel specimen for a test period of 24 h, followed by a visual inspection for rusting. Similar test procedures exist for inhibited fuel products.

The testing of inhibitors for use in oil and gas production, transport and processing normally involves two-phase oil-water fluids with, sometimes, a

solid phase, e.g. entrained sand particles. Tests are usually of the dynamic variety with continuous movement so that test specimens contact all phases present. A well known laboratory test procedure is the so-called wheel test in which bottles of about 200 cm³ volume containing weighed test specimens and a two-phase fluid saturated with an appropriate gas (CO₂ or H₂S) rotate inside a temperature-controlled chamber³⁴⁴. For many applications in these technologies data are required for high-temperature high-pressure conditions, and the use of autoclaves then becomes essential³⁴⁵. Two reviews on test procedures for corrosion inhibitors have been published^{346,347}.

Vapour Phase Conditions

The testing of vapour phase inhibitors, usually referred to as volatile corrosion inhibitors, is essentially a matter of placing a test specimen in the vapour space of a closed vessel containing an aggressive atmosphere—frequently water vapour, perhaps with SO₂ present—and a quantity of the inhibitor. Variations on the basic technique include provision for circulation of the vapour, the use of paper impregnated with inhibitor, provision for temperature cycling, etc.

In the early 1950s, Wachter *et al.*³⁴⁸, in the USA, described a humidity cabinet test in which metal specimens were supported inside inverted glass tubes containing a slip of inhibitor-impregnated paper in the lower end. The test was conducted at 37.7°C and 100% r.h. In the UK, Stroud and Vernon³⁴⁹ described two types of test: (1) with a single test specimen suspended from a cork in the neck of a 250 cm³ conical flask containing 25 cm³ of water with 5 mass% of the inhibitor which was held at 35°C during the day and at room temperature overnight, and (2) with specimens suspended in the upper part of glass tubes containing water and inhibitor with the lower part of the tubes immersed in a thermostatted bath so that condensation occurred in the upper part of the tubes. Other forms of test using a climatic cabinet with tropical or industrial atmospheres have also been described³⁵⁰.

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19.1A Appendix—Chemical and Electrochemical Methods for the Removal of Corrosion Products

This appendix provides information on chemical and electrochemical treatments which have been recommended for the removal of corrosion products. In using these methods the following points need to be borne in mind:

1. The duration of chemical or electrochemical treatment should be kept to the minimum necessary to remove the corrosion product. Loosely adherent material should be removed beforehand by suitable mechanical means, e.g. scrubbing.

2. The combined action of chemical (or electrochemical) treatment and scrubbing is often more effective than either method alone. It is frequently advantageous to alternate short periods of immersion with scrubbing to remove any corrosion product that has become loosened by the action of the chemical reagent.

3. The rate of attack of the chemical reagent on sound metal should be determined on a separate uncorroded sample of the material being cleaned, and if necessary a correction should be applied to the loss in weight of the corroded specimen. However, where a metal, and particularly an alloy, is heavily corroded—thus exposing a different surface structure from that of an uncorroded surface—it will be necessary to check the reliability of the cleaning method [Mercer, A. D., Butler, G. and Warren, G. M., *Br. Corros. J.*, 12, (2), 122–126 (1977)]. A procedure for obtaining more accurate weight loss data in these circumstances has been described [ISO/DIS 8407.2:1989].

4. The possibility of redeposition of metal from the dissolved corrosion product or, if electrochemical treatment is employed, from the anode material should always be kept in mind. If there is reason to believe this has occurred during removal of the corrosion product, further treatment to remove the redeposited metal will be necessary before the weight loss due to corrosion is measured.

Procedures for Removing Corrosion Products

The removal of corrosion products from metal specimens is described in Reference 1 and in ASTM RG1:1988 and ISO/DIS 8407.2:1989 and certain of these procedures are described below.

Electrolytic Cathodic Cleaning

After scrubbing to remove loosely attached corrosion products, cathodically polarise in hot dilute sulphuric acid under the following conditions:

Electrolyte—sulphuric acid (5% wt.%) plus an inhibitor (0.5 kg m^{-3}) such as diorthotolyl thiourea, quinoline ethiodide or β -naphthol quinoline. The temperature should be 75°C , the cathode current density 2000 Am^{-2} and the time of cathodic polarisation 3 min. The anode should be carbon or lead. If lead anodes are used, lead may deposit on the specimens and cause an error in the weight loss. If the specimen is resistant to nitric acid the lead may be removed by a flash dip in 1:1 nitric acid. Except for this possible source of error, lead is preferred as an anode, as it gives more efficient corrosion product removal.

After the electrolytic treatment, scrub the specimen with a brush, rinse thoroughly and dry.

Electric treatment may result in the redeposition of a metal, such as copper, from reducible corrosion products, and thus decrease the apparent weight loss.

Chemical Cleaning

Copper and nickel alloys Dip for 1–3 min in 1:1 HCl or 1:10 H_2SO_4 at room temperature. Scrub lightly with bristle brush under running water, using fine scouring powder if needed.

Aluminium alloys Dip for 5–10 min in an aqueous solution containing 2 wt.% chromic acid (CrO_3) plus 5 vol.% orthophosphoric acid (H_3PO_4 , 85%) maintained at 80°C . Ultrasonic agitation will facilitate this procedure.

Rinse in water to remove the acid, brush very lightly with a soft bristle brush to remove any loose film, and rinse again. If film remains, immerse for 1 min in concentrated nitric acid and repeat previous steps. Nitric acid may be used alone if there are no deposits. (See comments on this method when used for corroded specimens in the paper by Mercer, A. D., Butler, G. and Warren, G. M., *Br. Corros. J.*, 12, 122 (1977).)

Tin alloys Dip for 10 min in boiling trisodium phosphate solution (15%). Scrub lightly with bristle brush under running water, and dry.

Lead alloys Preferably use the electrolytic cleaning procedure just described. Alternatively, immerse for 5 min in boiling 1% acetic acid. Rinse in water to remove the acid and brush very gently with a soft bristle brush to remove any loosened matter.

Alternatively, immerse for 5 min in hot 5% ammonium acetate solution, rinse and scrub lightly. This removes PbO and PbSO₄.

Zinc Immerse the specimens in warm (60–80°C) 10% NH₄Cl for several minutes. Then rinse in water and scrub with a soft brush. Then immerse the specimens for 15–20 s in a boiling solution containing 5% chromic acid and 1% silver nitrate. Rinse in hot water and dry.

Note: in making up the chromic acid solution it is advisable to dissolve the silver nitrate separately and add it to the boiling chromic acid to prevent excessive crystallisation of the silver chromate. The chromic acid must be free from sulphate to avoid attack on the zinc. Immerse each specimen for 15 s in a 6% solution of hydriodic acid at room temperature to remove the remaining corrosion products. Immediately after immersion in the acid bath, wash the samples first in tap water and then in absolute methanol, and dry in air. This procedure removes a little of the zinc and a correction may be necessary.

Magnesium alloys Dip for approximately 1 min in boiling 15% chromic acid to which has been added with agitation 1% silver chromate solution.

Iron and steel Preferably use the electrolytic cleaning procedure, or else immerse in Clark's solution (hydrochloric acid 100 parts, antimonious oxide 2 parts, stannous chloride 5 parts) for up to 25 min. The solution may be cold but it should be vigorously stirred. Remove scales formed under oxidising conditions on steel in 15 vol.% concentrated phosphoric acid containing 0.15 vol.% of an organic inhibitor at room temperature.

Stainless steels Clean stainless steels in 20% nitric acid at 60°C for 20 min. In place of chemical cleaning, use a brass scraper or brass bristle brush or both, followed by scrubbing with a wet bristle brush and fine scouring powder.

Other methods of cleaning iron and steel include immersion in molten sodium hydride and cathodic treatment in molten caustic soda. These methods may be hazardous to personnel, and should not be carried out by the uninitiated, or without professional supervision.

General Note

Whatever cleaning method is used, the possibility of removal of solid metal is present. This will result in error in the determination of the corrosion rate. One or more cleaned and weighed specimens should be recleaned by the same method and reweighed. Loss due to this second treatment may be used as a correction to that indicated by the first weighing.

F. L. LaQUE

19.1B Appendix—Standards for Corrosion Testing*

British Standards

BS 1224:1970	Specification for electroplated coatings of nickel and chromium
BS 1615:1987	Method of specifying anodic oxidation coatings on aluminium and its alloys
BS 1872:1984	Specification for electroplated coatings of tin
BS 2000:Part 135:1983	Rust-preventing characteristics of steam-turbine oil in the presence of water
BS 2011:	Environmental testing
Part 2.1	Tests
Ka:1982	Test Ka. Salt mist
Kb:1987	Test Kb. Salt mist, cyclic (sodium chloride solution)
Kc:1977	Test Kc. Sulphur dioxide test for contacts and connections
Kd:1977	Test Kd. Hydrogen sulphide test for contacts and connections
BS 3597:1984	Specification for electroplated coatings of 65/35 tin/nickel alloy
BS 3745:1970 (1988)	Method for the evaluation of results of accelerated corrosion tests on metallic coatings
BS 3900:	Methods of test for paints
Part E6:1974 (1989)	Cross-cut test
Part E10:1979 (1989)	Pull-off test for adhesion
Part F3:1971 (1986)	Resistance to artificial weathering (enclosed carbon arc) and Addendum No. 1
Part F4:1968 (1985)	Resistance to continuous salt spray
Part F6:1976 (1984)	Notes for guidance on the conduct of natural weathering test

* Corrosion standards, including test methods, in use in Europe, including national, ISO, ASTM, NACE and CEN documents up to the year 1990 are described in the conference proceedings 'Corrosion Standards: European and International Developments', P. McIntyre and A. D. Mercer, eds, The Institute of Metals, London (1991).

Part F8:1976 (1986)	Determination of resistance to humid atmospheres containing sulphur dioxide
Part F9:1982 (1985)	Determination of resistance to humidity (continuous condensation)
Part F12:1985	Determination of resistance to cathodic disbonding of coatings for use in marine environments
Part F13:1986	Filiform corrosion test on steel
Part G5:1976 (1984)	Determination of resistance to liquids
BS 4292:	Method for specifying electroplated coatings of gold and gold alloys
Part 1:1989	Gold and gold alloys for engineering purposes
BS 5117:	Testing corrosion inhibiting, engine coolant concentrate ('antifreeze')
Part 2:	Methods of test for corrosion inhibition performance
Section 2.1:1985 (1989)	General procedures
Section 2.2:1985 (1989)	Glassware tests
Section 2.3:1985 (1989)	Recirculating rig test
Section 2.4:1985 (1989)	Static engine test
Section 2.5:1985 (1989)	Field test
BS 5466:	Methods for corrosion testing of metallic coatings
Part 1:1977 (1988)	Neutral salt spray test (NSS test)
Part 2:1977 (1988)	Acetic acid salt spray test (ASS test)
Part 3:1977 (1988)	Copper-accelerated acetic acid salt spray test (CASS test)
Part 4:1979	Thioacetamide test (TAA test)
Part 5:1979	Corrodokote test (CORR test)
Part 6:1982	Rating the results of corrosion tests on electroplated coatings cathodic to the substrate
Part 7:1982	Guidance on stationary outdoor exposure corrosion tests
Part 8:1986	Sulphur dioxide test with general condensation of moisture
Part 9:1986	Saline droplets corrosion test (SD test)
BS 5735:1979	Test methods for determining electrolytic corrosion with electrical insulating materials
BS 5903:1980 (1987)	Method for determination of resistance to intergranular corrosion of austenitic stainless steels: copper sulphate-sulphuric acid method (Moneypenny Strauss test)
BS 6137:1982	Specification for electroplated coatings of tin/lead alloys
BS 6580:1985	Specification for corrosion inhibiting, engine coolant concentrate ('antifreeze')
BS 6682:1986	Method for the determination of bimetallic corrosion in outdoor exposure corrosion tests

BS 6918:1990	Glossary of terms for corrosion of metals and alloys
BS 6980:	Stress corrosion testing
Part 1:1988	Guide to testing procedures
Part 2:1990	Method for the preparation and use of bent-beam specimens
Part 3:1990	Method for the preparation and use of U-bend specimens
Part 4:1990	Method for the preparation and use of uniaxially loaded tension specimens
Part 5:1990	Method for the preparation and use of C-ring specimens
Part 6:1990	Method for the preparation and use of pre-cracked specimens
Part 7:1990	Method for slow strain rate testing

ASTM Standards

A 262:1986	Practices for detecting susceptibility to intergranular attack in austenitic stainless steels
A 708:1979	Recommended practice for detection of susceptibility to intergranular corrosion in severely sensitised austenitic stainless steel (intent to withdraw)
A 763:1986	Practice for detecting susceptibility to intergranular attack in ferritic stainless steels
B 117:1990	Method of salt spray (fog) testing
B 154:1987	Method for mercurous nitrate test for copper and copper alloys
B 368:1985	Method for copper-accelerated acetic acid-salt spray (fog) testing (CASS test)
B 380:1985	Methods for corrosion testing of decorative chromium electroplating by the Corrodokote procedure
B 457:1967 (1980)	Method for measurement of impedance of anodic coatings on aluminium
B 537:1970 (1980)	Recommended practice for rating of electroplated panels subjected to atmospheric exposure
B 735:1984	Test method for porosity in gold platings on metal substrates by gas exposures
C 876:1987	Test method for half-cell potentials of uncoated reinforcing steel in concrete
D 130:1988	Method for detection of copper corrosion from petroleum products by the copper strip tarnish test
D 610:1985	Method for evaluating degree of rusting on painted steel surfaces
D 714:1987	Method for evaluating degree of blistering of paints

D 807:1982	Method of assessing the tendency of industrial boiler waters to cause embrittlement (USBM embrittlement detector method)
D 849:1988	Test method for copper corrosion of industrial aromatic hydrocarbons
D 1014:1983 (1988)	Method for conducting exterior exposure tests of paints on steel
D 1280:1989	Method for total immersion corrosion test for soak tank metal cleaners
D 1374:1989	Method for aerated total immersion corrosion test for metal cleaners
D 1384:1987	Method for corrosion test for engine coolants in glassware
D 1611:1981 (1986)	Test method for corrosion produced by leather in contact with metal
D 1654:1979a (1984)	Method for evaluation of painted or coated specimens subjected to corrosive environments
D 1743:1987	Test method for corrosion preventive properties of lubricating greases
D 1748:1983	Test method for rust protection by metal preservatives in the humidity cabinet
D 1838:1984	Test method for copper strip corrosion by liquefied petroleum (LP) gases
D 2059:1987	Test method for resistance of zippers to salt spray (fog)
D 2247:1987	Practice for testing water resistance of coatings in 100% relative humidity
D 2251:1985	Test method for metal corrosion by halogenated organic solvents and their admixtures
D 2570:1985	Method for simulated service corrosion testing of engine coolants
D 2688:1983	Test method for corrosivity of water in the absence of heat transfer (weight loss methods)
D 2758:1986	Method of testing engine coolants by engine dynamometer
D 2776:1979	Test methods for corrosivity of water in the absence of heat transfer (electrical methods)
D 2803:1982 (1987)	Test method for filiform corrosion resistance of organic coatings
D 2809:1989	Test method for cavitation erosion-corrosion characteristics of aluminium pumps with engine coolants
D 2847:1985	Practice for testing engine coolants in car and light truck service
D 2933:1974 (1986)	Test method for corrosion resistance of coated steel specimens (cyclic method)
D 2943:1986	Method of aluminium scratch test for 1,1,1-trichloroethane

D 3262:1982	Test methods for corrosivity of solvent systems for removing water-formed deposits
D 3310:1974 (1983)	Recommended practice for determining corrosivity of adhesive materials
D 3842:1986	Guide to the selection of test methods for coatings used in light-water nuclear power plants
D 3843:1980	Practice for quality assurance for protective coatings applied to nuclear facilities
D 3911:1980	Method for evaluating coatings used in light-water nuclear power plants at simulated loss of coolant accident (LOCA) conditions
D 3912:1980 (1985)	Test method for chemical resistance of coatings used in light-water nuclear power plants
D 3929:1980 (1984)	Practice for evaluating the stress cracking of plastics by adhesives using the bent-beam method
D 4340:1989	Test method for corrosion of cast aluminium alloys in engine coolants under heat-transfer conditions
D 4350:1986	Test method for corrosivity index of plastics and fillers
D 4627:1986	Test method for iron chip corrosion test for water soluble metalworking fluids
D 4798:1988	Test method for accelerated weathering test conditions and procedures for bituminous materials (xenon-arc method)
E 647:1988a	Test method for measurement of fatigue crack growth rates
F 363:1979 (1985)	Method for corrosion testing of enveloped gaskets
F 482:1984	Method for total immersion corrosion test for tank-type aircraft maintenance chemicals
F 483:1977	Method for total immersion corrosion test for aircraft maintenance chemicals
F 981:1987	Practice for assessment of compatibility of bio-materials (non-porous) for surgical implants with respect to effect of materials in muscle and bone
F1110:1988	Test method for sandwich corrosion test
G 1:1988	Recommended practice for preparing, cleaning, and evaluating corrosion test specimens
G 2:1988	Practice for aqueous corrosion testing of samples of zirconium and zirconium alloys
G 2M:1988	Test method for corrosion testing of products of zirconium, hafnium and their alloys in water at 633 K or in steam at 673 K [metric]
G 3:1989	Recommended practice for conventions applicable to electrochemical measurements in corrosion testing

G 4:1984	Guide for conducting corrosion coupon tests in plant equipment
G 5:1987	Standard reference test method for making potentiostatic and potentiodynamic anodic polarisation measurements
G 7:1989	Recommended practice for atmospheric environmental exposure testing of nonmetallic materials
G 11:1983	Test method for effects of outdoor weathering on pipeline coatings
G 15:1989a	Definitions of terms relating to corrosion and corrosion testing
G 16:1971 (1984)	Recommended practice for applying statistics to analysis of corrosion data
G 23:1989	Practice for operating light- and water-exposure apparatus (carbon-arc Type) for exposure of nonmetallic materials
G 28:1985	Method for detecting susceptibility to intergranular attack in wrought nickel-rich, chromium-bearing alloys
G 30:1979 (1984)	Practice for making and using U-bend stress corrosion test specimens
G 31:1972 (1985)	Recommended practice for laboratory immersion corrosion testing of metals
G 32:1985	Method for vibratory cavitation erosion test
G 33:1988	Practice for recording data from atmospheric corrosion tests of metallic-coated steel specimens
G 34:1986	Test method for exfoliation corrosion susceptibility in 2XXX and 7XXX series aluminium alloys (EXCO test)
G 35:1988	Practice for determining the susceptibility of stainless steels and related nickel-chromium-iron alloys to stress corrosion cracking in polythionic acids
G 36:1987	Recommended practice for performing stress corrosion cracking tests in a boiling magnesium sulphate solution
G 37:1985	Test method for use of Mattsson's solution of pH 7.2 to evaluate the stress corrosion cracking susceptibility of copper-zinc alloys
G 38:1973 (1984)	Practices for making and using C-ring stress corrosion cracking test specimens
G 39:1979 (1984)	Practice for preparation and use of bent-beam stress corrosion specimens
G 41:1985	Test method for determining cracking susceptibility of metals exposed under stress to a hot salt environment
G 44:1988	Practice for alternate immersion stress corrosion testing in 3.5% sodium chloride solution

G 46:1976 (1986)	Recommended practice for examination and evaluation of pitting corrosion
G 47:1979 (1984)	Test method for determining susceptibility to stress corrosion cracking of high-strength aluminium alloy products
G 48:1976 (1980)	Test method for pitting and crevice corrosion resistance of stainless steels and related alloys by the use of ferric chloride solution
G 49:1985	Recommended practice for preparation and use of direct tension stress corrosion test specimens
G 50:1976 (1984)	Recommended practice for conducting atmospheric stress corrosion tests on metals
G 51:1977 (1984)	Test method for pH of soil for use in corrosion testing
G 52:1988	Practice for exposing and evaluating metals and alloys in surface seawater
G 57:1978 (1984)	Method for field measurement of soil resistivity using the Wenner four-electrode method
G 58:1985	Practice for the preparation of stress corrosion test specimen for weldments
G 59:1978 (1984)	Practice for conducting potentiodynamic polarisation resistance measurements
G 60:1986	Method for conducting cyclic humidity tests
G 61:1986	Test method for conducting cyclic potentiodynamic polarisation measurements for localised corrosion susceptibility of iron-, nickel-, or cobalt-based alloys
G 64:1985	Classification of resistance to stress corrosion cracking of high-strength aluminium alloys
G 66:1986	Method for visual assessment of exfoliation corrosion susceptibility of 5XXX series aluminium alloys (Asset test)
G 67:1986	Test method for determining the susceptibility to intergranular corrosion of 5XXX series aluminium alloys by mass loss after exposure to nitric acid (NAMLT test)
G 68:1980	Practice for liquid sodium corrosion testing of metals and alloys
G 69:1981	Practice for measurement of corrosion potentials of aluminium alloys
G 71:1981 (1986)	Practice for conducting and evaluating galvanic corrosion tests in electrolytes
G 73:1982 (1987)	Practice for liquid impingement erosion testing
G 78:1989	Guide for crevice corrosion testing of iron base and nickel base stainless steels in seawater and other chloride-containing aqueous environments

G 82:1983	Guide for development and use of a galvanic series for predicting galvanic corrosion performance
G 84:1989	Practice for measurement of time-of-wetness on surfaces exposed to wetting conditions as in atmospheric corrosion testing
G 85:1984	Practice for modified salt spray (fog) testing
G 87:1984	Practice for conducting moist SO ₂ tests
G 90:1985	Practice for performing accelerated outdoor weathering of nonmetallic materials using concentrated natural sunlight
G 91:1986	Test Method for monitoring atmospheric SO ₂ using sulfation plate technique
G 92:1986	Practice for characteristics of atmospheric test sites
G 100:1989	Method for conducting cyclic galvanostair-case polarisation
G 101:1989	Guide for estimating the atmospheric corrosion resistance of low-alloy steels
G 102:1989	Practice for calculation of corrosion rates and related information from electrochemical measurements
G 103:1989	Method for performing a stress-corrosion cracking test of low copper containing Al-Zn-Mg alloys in boiling 6% sodium chloride solution
G 104:1989	Test method for assessing galvanic corrosion caused by the atmosphere

International Standards

ISO 2160:1985	Petroleum products–corrosiveness to copper. Copper strip test
ISO 2810:1974	Notes for guidance on the conduct of natural weathering tests
ISO 3651-1:1976	Austenitic stainless steels–determination of resistance to intergranular corrosion. Part 1: Corrosion test in nitric acid medium by measurement of loss of mass (Huey test)
ISO 3651-2:1976	Austenitic stainless steels–determination of resistance to intergranular corrosion. Part 2: Corrosion test in a sulphuric acid/copper sulphate medium in the presence of copper turnings (Moneypenny Strauss test)
ISO 3768:1976	Neutral salt spray test
ISO 3769:1976	Acetic acid salt spray test
ISO 3770:1976	Copper accelerated acetic acid salt spray test
ISO 4536:1985	Saline droplet test
ISO 4538:1978	Thioacetamide corrosion test

ISO 4539:1980	Electrodeposited chromium coatings. Electrolytic corrosion testing
ISO 4540:1980	Coatings cathodic to the substrate—rating of electroplated test specimens subjected to corrosion tests
ISO 4541:1978	Corrodokote corrosion test
ISO 4542:1981	General rules for stationary outdoor exposure corrosion tests
ISO 4543:1981	General rules for corrosion tests applicable to storage conditions
ISO 4623:1984	Filiform corrosion test on steel
ISO 6251:1982	Liquefied petroleum gases—corrosiveness to copper. Copper strip test
ISO 6314:1980	Road vehicles—brake linings—resistance to water, saline solution, oil and brake fluid—test procedure
ISO 6315:1980	Road vehicles—brake linings—seizure to ferrous mating surfaces due to corrosion—test procedure
ISO 6505:1984	Rubber vulcanised—determination of adhesion to, and corrosion of, metals
ISO 6509:1981	Corrosion of metals and alloys; determination of dezincification resistance of brass
ISO 6988:1985	Sulphur dioxide test with general condensation of moisture
ISO 7120:1987	Petroleum products and lubricants—petroleum oils and other fluids—determination of rust preventing characteristics in the presence of water
ISO 7384:1986	Corrosion tests in artificial atmosphere; general requirements
ISO 7441:1989	Corrosion of metals and alloys; determination of bimetallic corrosion in outdoor exposure corrosion tests
ISO 7539-1:1987	Corrosion of metals and alloys; stress corrosion testing. Part 1: General guidance on testing procedures
ISO 7539-2:1989	Corrosion of metals and alloys; stress corrosion testing. Part 2: Bent-beam specimens
ISO 7539-3:1989	Corrosion of metals and alloys. Part 3: U-bend specimens
ISO 7539-4:1989	Corrosion of metals and alloys. Part 4: Uniaxially loaded tensile specimens
ISO 7539-5:1989	Corrosion of metals and alloys. Part 5: C-ring specimens
ISO 7539-6:1990	Corrosion of metals and alloys. Part 6: Pre-cracked specimens
ISO 7539-7:1989	Corrosion of metals and alloys. Part 7: Slow strain rate stress corrosion tests
ISO/8044:1986	Terms for corrosion of metals and alloys

ISO/DIS 8407.2:1989	Metals and alloys; removal of corrosion products from corrosion test specimens
ISO 8565:1992	Metals and alloys; atmospheric corrosion testing; general requirements for field tests
ISO/DIS 9223:1990	Corrosion of metals and alloys. Classification of corrosivity of atmospheres
ISO/DIS 9224:1990	Corrosion of metals and alloys. Guiding values for the corrosivity categories of atmospheres
ISO/DIS 9225:1990	Corrosion of metals and alloys. Corrosivity of atmospheres. Methods of measurement of pollution
ISO/DIS 9226:1990	Corrosion of metals and alloys. Methods for the determination of corrosion rate of standard specimens for the evaluation of corrosivity
ISO/DIS 9227.2:1989	Corrosion tests in artificial atmospheres; salt spray tests
ISO/DIS 9400:1989	Nickel-based alloys—Determination of resistance to intergranular corrosion
ISO/DIS 10062:1990	Corrosion tests in artificial atmospheres at very low concentrations of polluting gas(es)
IEC 68-2-42:1982	Test K_c —sulphur dioxide test for contacts and connectors
IEC 68-2-43:1976	Test K_d —hydrogen sulphide test for contacts and connections
IEC 68-2-46:1982	Guidance to test K_d
IEC 68-2-60:1980	Test K_c —corrosion tests in artificial atmosphere at very low concentrations of polluting gases

NACE Standards

NACE TM 0169-76	Laboratory corrosion testing of metals for the process industries
NACE TM 0170-70	Visual standard for surfaces of new steel airblast cleaned with sand abrasive
NACE TM 0171-71	Autoclave corrosion testing of metals in high temperature water
NACE TM 0172-86	Antirust properties of cargoes in petroleum product pipelines
NACE TM 0174-74	Laboratory methods for the evaluation of protective coatings used as lining materials in immersion service
NACE TM 0177-86	Testing of metals for resistance to sulphide stress cracking at ambient temperatures
NACE TM 0184-88	Accelerated test procedures for screening atmospheric surface coating systems for off-shore platforms and equipment

NACE TM 0270-72	Method of conducting controlled velocity laboratory corrosion tests
NACE TM 0274-74	Dynamic corrosion testing of metals in high temperature water
NACE TM 0275-89	Performance testing of steel and reinforced plastic sucher rods by the mixed string alternate rod method
NACE TM 0286-88	Cooling water test units incorporating heat transfer surfaces

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19.2 The Potentiostat and its Application to Corrosion Studies

The potentiostatic technique discussed here involves the polarisation of a metal electrode at a series of predetermined constant potentials. Potentiostats have been used in analytical chemistry for some time¹; Hickling² was the first to describe a mechanically controlled instrument and Roberts³ was the first to describe an electronically controlled instrument. Greene⁴ has discussed manual instruments and basic instrument requirements.

The determination of polarisation curves of metals by means of constant potential devices has contributed greatly to the knowledge of corrosion processes and passivity. In addition to the use of the potentiostat in studying a variety of mechanisms involved in corrosion and passivity, it has been applied to alloy development, since it is an important tool in the accelerated testing of corrosion resistance. Dissolution under controlled potentials can also be a precise method for metallographic etching or in studies of the selective corrosion of various phases. The technique can be used for establishing optimum conditions of anodic and cathodic protection. Two of the more recent papers have touched on limitations in its application⁵, and differences between potentiostatic tests and exposure to chemical solutions⁶.

In this section an attempt is made to give a more detailed introduction to experimental procedures, as well as to some of the ideas where the use of the potentiostat has helped in the understanding of corrosion processes.

Experimental Apparatus

Instruments very suitable for corrosion work are readily available, with several different models produced commercially. Although most, if not all, of the available potentiostats are properly designed, it should be kept in mind that corrosion studies require the instrument to have a low internal resistance and to react quickly to changes of potential of the working electrode.

A basic circuit is shown schematically in Fig. 19.36(a). The specimen C., or working electrode W.E. is the metal under study, the auxiliary electrode A.E. is usually platinum and R.E. is the reference electrode, for instance a saturated calomel electrode. The desired potential difference between the specimen and the reference electrode is set with the backing circuit B. Any

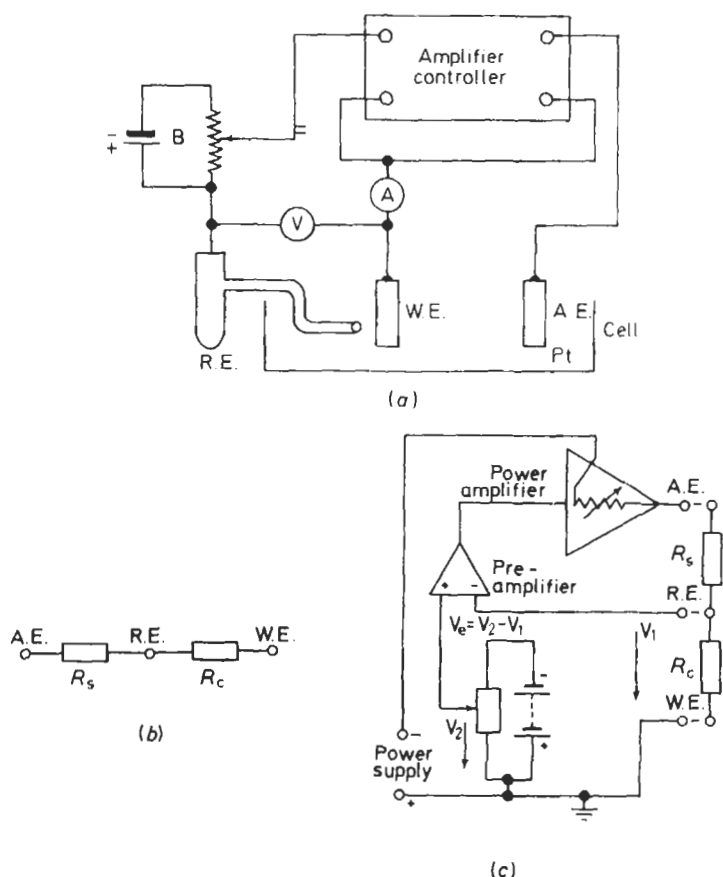


Fig. 19.36 Basic circuit for a potentiostat. (a) Basic circuit for a potentiostat and electrochemical cell. (b) Equivalent circuit. (c) Circuit of a basic potentiostat. A.E. is the auxiliary electrode, R.E. the reference electrode and W.E. the working electrode (b and c are from *Potentiostat and its Applications* by J. A. von Fraunhofer and C. H. Banks, Butterworths (1972))

unbalance between the electrode potential and the backing potential produces an error signal at the input of the amplifier-controller circuit. The latter rapidly adjusts the cell current between the specimen and the auxiliary electrode until the error signal is reduced to zero.

The electrical characteristics of the cell and electrode will comprise both capacitative and resistive components, but for simplicity the former may be neglected and the system can be represented by resistances in series (Fig. 19.36b and c). The resistance R_s simulates the effective series resistance of the auxiliary electrode A.E. and cell solution, whilst the potential developed across R_c by the flow of current between the working electrode W.E. and A.E. simulates the controlled potential W.E. with respect to R.E.

Figure 19.36c shows a basic circuit of a potentiostat in which the difference between the desired potential (V_2) and the actual potential of the working

electrode (V_1) is amplified by a high gain differential pre-amplifier. The output is an error signal $AV_e = A(V_2 - V_1)$, where A is the gain of the amplifier, which is arranged to control the power amplifier in such a way that the potential of A.E. is continuously adjusted to minimise V_e . If the loop gain is high, V_e can be made to approach zero very closely, the limit being determined by the electrical noise in the system. The potential of W.E. with respect to R.E. is thus held constant at the desired potential, V_2 .

When potential setting is varied manually during the determination of polarisation, each change can be made after a constant time interval or when the rate of current change reaches a predetermined low level. A number of instruments for programmed potential changes have been introduced, permitting a variety of continuous sweeps or stepwise traverses over a desired range of potential. This, together with a suitable electrometer, recorder, noise filter (when necessary) and logarithmic converter, provide an automated procedure for plotting E -log i curves.

An ASTM recommended practice (*A Standard Reference Method for Making Potentiostatic and Potentiodynamic Anodic Polarisation Measurements*, G5:1972) has been issued. It provides a means of checking experimental technique and instrumentation using a specimen from a single heat of AISI Type 430 stainless steel, which is available from ASTM*.

Scanning Rate

The time factor in stepwise potentiostatic or potentiodynamic polarisation experiments is very important, because large differences can be caused by changes in the scanning rate. Since the steady state depends on the particular system and conditions of exposure, no set rule exists for the magnitude or frequency of potential changes. Chatfield *et al.*^{6a} have studied the Ni/H₂SO₄ system and have shown how E_{pass} becomes more passive with increase in sweep rate.

In order for the potentiostatic technique to provide an accelerated test, whether for general or localised corrosion, it is obvious that an accelerating factor is needed. Merely duplicating service conditions by substituting the potentiostat for chemical potential control does not necessarily shorten the required testing time. When employing an accelerating factor, such as higher temperature, change in chemistry of the environment, or a greater driving force (potential), care should be taken to ensure that the mechanism of the reaction(s) under examination is not altered.

***iR* Corrections, Probe Positioning, Specimen Masking and Mounting**

There is no difference between galvanostatic and potentiostatic polarisation experiments regarding the iR potential drop between the specimen and the tip of the probe used for measuring the electrochemical potential. In either case corrections should be made for accuracy. These could be quite large if the current density is high and/or the conductivity of the electrolyte is low.

* American Society for Testing and Materials, Headquarters, 1916 Race Street, Philadelphia, Pa., USA.

The position of the probe relative to the test specimen surface can cause differences in potential readings⁷.

Adequate specimen masking is one of the major problems in corrosion testing. Crevices with non-uniform current distribution and in which changes in the chemistry of the electrolyte can take place rapidly, are particularly undesirable⁸. In potentiostatic work, pitting or crevice attack is frequently found near the masking interface (or under it when seepage and undermining occur). Unless this factor is specifically being investigated, it should be avoided. The use of a partially immersed specimen can eliminate the need for masking, although it leaves the water line to be dealt with. A method for mounting a cylindrical specimen has been described^{9,10}, which avoids crevices when the holder is properly tightened (*see* Section 19.7). Specimens can also be rotated during the test, if desired, when this method is used.

Applications

Studies of Passivity

The potentiostat is particularly useful in determining the behaviour of metals that show active-passive transition. Knowledge of the nature of passivity and the probable mechanisms involved has accumulated more rapidly since the introduction of the potentiostatic technique. Perhaps of more importance for the subject at hand are the practical implications of this method. We now have a tool which allows an 'operational' definition of passivity and a means of determining the tendency of metals to become passive and resist corrosion under various conditions.

The use of the potentiostatic method has helped to show that the process of self-passivation is practically identical to that which occurs when the metal is made anodically passive by the application of an external current¹¹⁻¹⁵. The polarisation curve usually observed is shown schematically in Fig. 19.37a. Without the use of a potentiostat, the active portion of the curve *AB* would make a sudden transition to the curve *DE*, e.g. along curve *AFE* or *AFD*, and observation of the part of the curve *BCDE* during anodic polarisation was not common until the potentiostat was used.

The current-potential relationship *ABCDE*, as obtained potentiostatically, has allowed a study of the passive phenomena in greater detail and the operational definition of the passive state with greater preciseness. Bonhoeffer, Vetter and many others have made extensive potentiostatic studies of iron which indicate that the metal has a thin film, composed of one or more oxides of iron, on its surface when in the passive state¹⁶⁻¹⁹. Similar studies have been made with stainless steel, nickel, chromium and other metals²⁰⁻²⁵.

Since the corrosion potential of a metal in a particular environment is a mixed potential — where the total anodic current is equal to the total cathodic current — the potentiostatic curve obtained by external polarisation will be influenced by the position of the local cathodic current curve. (Edeleanu²⁷ and Mueller²⁸ have discussed the details which must be considered in the analysis and interpretation of the curves.) For this reason, residual oxygen in the test solution can cause a departure from the usual curve; in such a

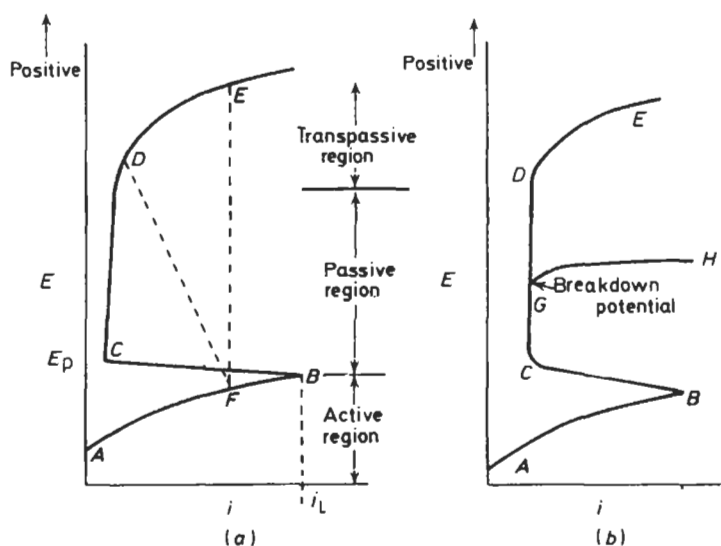


Fig. 19.37 Schematic polarisation curves from anodic potentiostatic polarisation

case, a 'negative loop' B' corresponding with cathodic reduction of dissolved oxygen occurs after passing the critical point, with the normal passive region and low positive currents only being resumed at E_{C_2} , as shown in Fig. 19.38. Other ions can also interfere with the currents observed. If they are oxidising, then they will have much the same effect as dissolved oxygen. However, some of them may increase the observed current to values that suggest corrosion rates much higher than are actually taking place. The

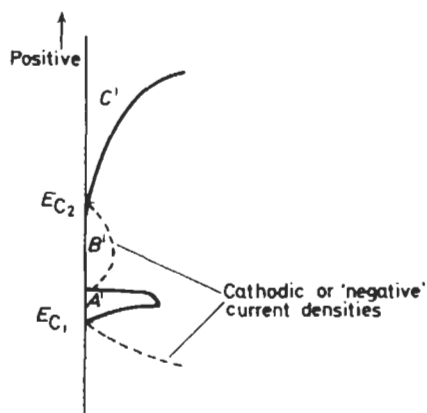


Fig. 19.38 Schematic polarisation from potentiostatic polarisation. B' shows the 'negative loop' and represents the cathodic reduction of dissolved oxygen. The dashed curves in the diagram are cathodic currents and are frequently drawn on the left-hand side of the E axis

polarisation curve for titanium²⁹ indicated current levels in the passive region that did not agree with the (lower) corrosion rates determined gravimetrically, and this was found to be due to the presence of Ti^{3+} ions in solution. In the case of iron in neutral water³⁰, the passive anodic current densities were found to be proportional to the concentration of Fe^{2+} . Indig³¹ observed similar current increases in stagnant high-temperature water tests due to the formation of Fe_2O_3 from Fe^{2+} ; he largely eliminated this by changing to a flowing electrolyte system, and achieved correlation with actual corrosion rates.

The critical current and primary passivation potential E_{pp} will not appear on an anodic polarisation curve when the steady-state potential already is higher than E_{pp} . In such a case the potentiostat is unable to provide direct data for constructing the full polarisation curve. If that portion of the curve below the steady-state potential is desired, then the potential has to be held constant at several points in this range and corrosion currents calculated from corrosion rates as determined from solution analyses and/or weight losses.

The potentiostat is very useful for determining the effects of composition and heat treatment on the corrosion resistance of alloys. Sometimes it is possible to understand what appear to be discrepancies in practice. Edeleanu²⁷ used the method for determining the resistance of stainless steels to acids. The potentiostatic curves showed that the current in the transpassive region (at a very high potential) increased with the chromium content, while the current in the passive region (at lower potentials) decreased. This explained the behaviour of several steels in service, where steels of higher chromium content showed poor resistance to corrosion in environments of high redox potentials—nitric acid plus chromic acid mixtures—but greater resistance in nitric acid. Edeleanu also discussed potentiostatic curves which showed the beneficial effects of nickel, copper and molybdenum on the corrosion resistance of stainless steel in sulphuric acid. This paper should be consulted for an excellent discussion on the use of these techniques for determining the effects of alloy composition on corrosion resistance.

Cihal, *et al.*³² presented early data on the effects of chromium, nickel, molybdenum, titanium, niobium and silicon on the passive behaviour of stainless steel.

Pitting

Some stainless steels and aluminium alloys are examples of metals that show pitting corrosion when exposed to aqueous solutions containing halide ions, although the phenomenon is not confined to these alloys. Various factors influence the onset of pitting, one of which is the interfacial potential; pits are thought to form only at potentials more positive than a certain critical value. This can be demonstrated by electrochemical measurements using potentiostatic techniques³³⁻⁴², and Fig. 19.37*b* which is similar to that shown by Kolotyrkin's⁴³, represents a typical curve. In the absence of aggressive (pitting) ions, *ABCDE* represents the usual polarisation behaviour, where *DE* is the region of transpassivity. However, when conditions suitable for

pitting prevail, the curve *ABCGH* is typically found, and the breakout (or breakthrough) *GH* from the passive region is accompanied by pitting. The first point of departure from the passive region has been referred to as the 'critical pitting potential', but it should be noted that its value is time dependent and that it varies with the rate of potential change, i.e. if the potential sweep rate or stepping rate is too rapid, a more positive 'critical' value is obtained. In general, the shorter the time the more positive is the 'critical pitting potential', and in order to be certain that a reliable estimate of the pitting potential has been made, it is necessary to hold the potential at a constant value just below the critical point for a suitably long time (in practice, several days*), in order to demonstrate retention of passivity and the absence of pits in the specimen surface (*see also* Section 1.6).

The correlation between the redox potential of a system and the occurrence of pitting attack was established some 30 years ago⁴⁴. Also, the use of passivity breakdown as a screening method for alloy resistance was described over the years by several workers, for example, Brenner⁴⁵, Mahla and Nielsen⁴⁶, and Pourbaix⁴⁷. For a metal in a given solution, it may appear that the electrochemical potential, regardless of its origin, will be the only determinant of whether or not pitting will take place. While this is generally expected, France and Greene⁶ suggested that a potentiostatically controlled corrosion test could be more severe than a conventional one (chemically controlled potential). Their reason is related to local chemistry changes required to preserve charge neutrality; during anodic polarisation migration of Cl^- ions occurs to balance the excess positive charge produced by the Fe^{2+} ions and this results in an increase of Cl^- ions at the metal/solution interface and a consequent increase in pitting propensity. A similar movement of anions in, for example, a solution of FeCl_3 , does not occur (*see also* Table 21.33). Figure 19.39 is taken from the work of France and Greene to illustrate the movement of Cl^- ions across a boundary line.

Correspondence between electrochemical tests and field exposures has not always been found. Therefore, it is difficult to interpret potentiostatic data in terms of service performance. Disagreement between results can be caused by factors that are not immediately obvious. For example, gases such as hydrogen, argon or nitrogen are generally used to remove oxygen from solution before proceeding with a potentiostatic test. At first sight, it might appear immaterial which gas is used, but Wilde and Williams⁴⁸ found differences in the breakout (critical pitting) potential of stainless steels, depending on the selection of gas.

More details of other factors that affect the critical pitting potential have been discussed by Uhlig and his co-workers^{49,50}. They indicated that for stainless steel the critical pitting potential decreased with increasing concentration of chloride ion. At a fixed chloride level, passivating ions in solution, such as sulphate and nitrate, etc., cause the pitting potential to become more positive; at a sufficient concentration these ions totally inhibited pitting, as shown in Fig. 19.40 for SO_4^{2-} and ClO_4^- .

Lizlovs and Bond⁵¹ reported a molar ratio of 5:1 ($\text{SO}_4^{2-}:\text{Cl}^-$) for inhibiting pitting in ferritic stainless steels. A plot of critical potential vs.

* Even after several days of no localised attack, the question could legitimately be asked whether the test was long enough to establish a true value, below which pitting would *never* occur.

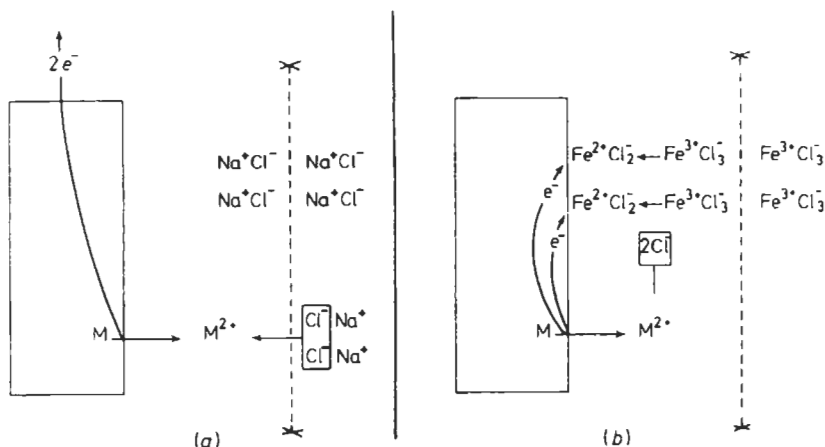


Fig. 19.39 Schematic representation of reactions during (a) controlled potential and (b) conventional corrosion tests in acidic chloride solutions. In (a) charge balance must be maintained by migration of Cl^- ions, since the cathodic reaction occurs elsewhere at the counter-electrode. In (b) the anodic and cathodic sites are in close proximity, and charge balance is maintained without migration of Cl^- ions from the bulk solution (after France and Greene⁶)

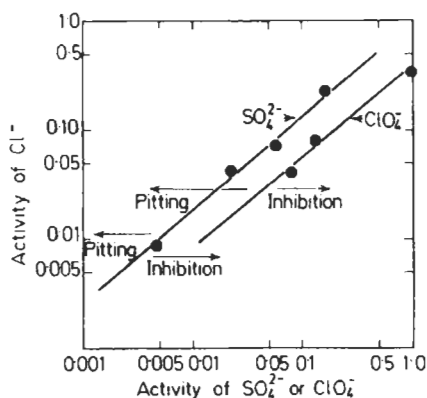


Fig. 19.40 Activity of SO_4^{2-} or ClO_4^- required to inhibit pitting as a function of Cl^- activity; 25°C (after Leckie and Uhlig⁴⁹)

ratio of $\text{S}_4^{2-}:\text{Br}^-$ is reproduced in Fig. 19.41 from the work of Kolo-tyrkin⁴³. Lowering the temperature causes the critical potential to become more positive⁴⁹. Changes of pH in the acid range did not affect the pitting potential appreciably, but in the alkaline region it increased markedly with pH, as shown in Fig. 19.42.

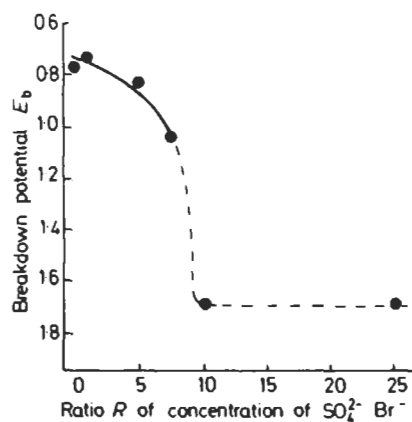


Fig. 19.41 Dependence of breakdown potential of Fe-Cr alloys (containing 13% Cr, in 0.1 mol dm^{-1} $\text{HBr} + \text{K}_2\text{SO}_4$ solution) on the ratio of sulphate and bromide concentration in solution (after Kolotykin⁴³)

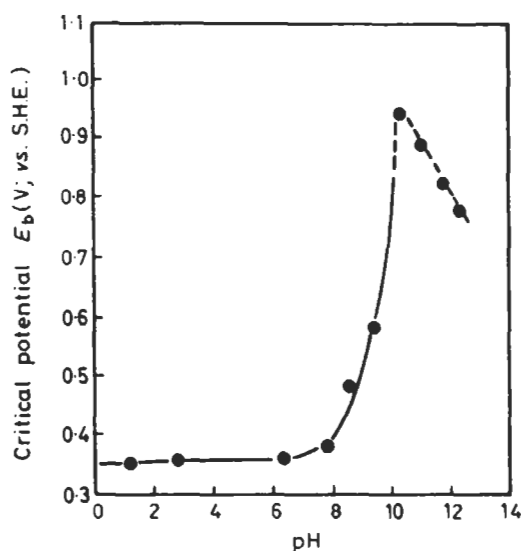


Fig. 19.42 Effect of pH on critical potential for pitting in 0.1 mol dm^{-1} NaCl ; 25°C (after Leckie and Uhlig⁴⁵)

The fact that scanning speed can affect polarisation behaviour has already been mentioned. In the case of stainless steel a plot of critical potential E_b vs. rate shows how E_b becomes more positive with potential change rate (Fig. 19.43)⁵². When a specimen was held at a fixed passive potential while aggressive ions (Cl^-) were added to determine the concentration required

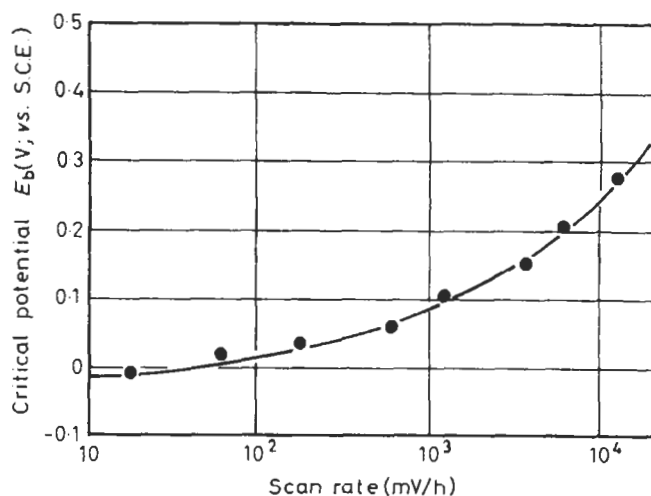


Fig. 19.43 Effect of potential scan rate on the value of E_b for Type 304 stainless steel in $0.1 \text{ mol dm}^{-3} \text{ NaCl}$ (after Leckie⁵²)

for loss of passivity (pitting), then a similar time effect was observed⁵³; a higher apparent resistance, i.e. greater apparent Cl^- ion tolerance, was found when making more rapid additions.

Numerous references regarding alloying additions have been published, and the reader should look up specific effects for relevant alloying systems.

Potential-pH Diagrams

Pourbaix has contributed substantially to the science of corrosion through plotting thermodynamic data of systems as a function of electrode potential and pH. Numerous publications of his have appeared in the literature, as well as an atlas of potential-pH diagrams. Reference 54 exemplifies the usefulness of potentiostatic polarisation curves in the experimental plotting of various domains, such as protection, pitting, general corrosion and passivity, in these diagrams. This particular procedure, which has been dealt with in some detail in Section 1.6, is a very powerful tool which is now available for studying corrosion.

De-alloying

The selective net loss of a component such as zinc, aluminium or nickel from copper-base alloys sometimes occurs when these alloys corrode. Early studies of the phenomenon were done by simple immersion. More recently, however, the potential-pH dependence of de-alloying has been examined⁵⁵, and it appears that this approach can provide a much more detailed understanding of the mechanism. Future experimental work is expected to include potentiostatic and potentiodynamic techniques to a much greater extent.

Selective Etching

Dissolution kinetics are influenced by pH, potential and the ions present in the test solution, and this forms the basis of selective metallographic etching techniques that have been used for some time^{32, 56, 57}. The potentiostat is often used to hold the potential of a multi-phase alloy constant at a level

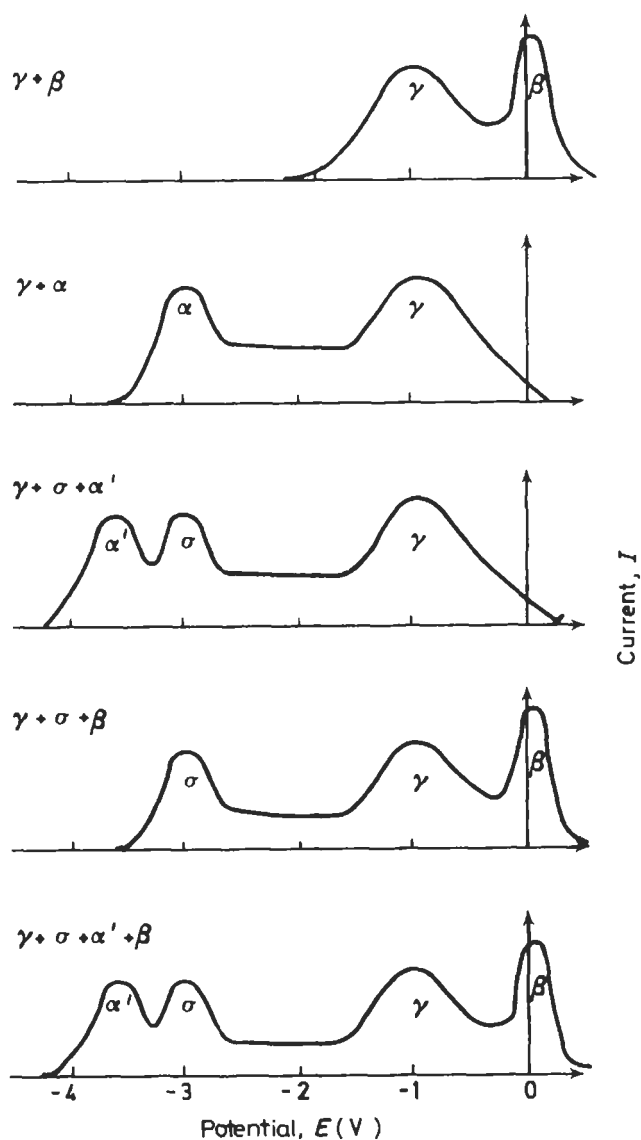


Fig. 19.44 Typical current vs. potential curves for alloys of various phase combinations (after Jones and Hume-Rothery⁵⁸)

suitable for attack on a specific phase while the rest of the surface remains passive. A scan over a potential range can be done as a preliminary step to ascertain whether the electrochemical properties of various phases differ sufficiently in the chosen electrolyte for selective etching or phase extraction. One such procedure was reported by Jones and Hume-Rothery⁵⁸ for austenitic steels alloyed with aluminium, and Fig. 19.44 is reproduced from their work. Another example is the behaviour of Fe-Fe₃C as a function of potential, pH and anion⁵⁹. In this latter work, the conditions were defined under which four different modes of attack took place, i.e. general-, matrix-, interface- and carbide attack, and the data were interpreted in terms of thermodynamics, kinetics and the influence of complex formation. These potentiostatic experiments were coupled with detailed electron transmission microscopy and the comprehensive nature of the results demonstrate the effectiveness of such a combined approach.

The extraction of precipitates for further examination is also possible by the same techniques. Conditions would have to be chosen to give matrix or interface attack.

Grain-boundary Corrosion

Intergranular corrosion is encountered in many metal systems, often associated with the presence of precipitates at grain boundaries. In the case of stainless steels, one widely accepted theory states that the precipitation of chromium carbides leads to a chromium-denuded zone which undergoes rapid corrosion.

Potentiostatic methods, being capable of detecting differences in corrosion and passivation behaviour of various parts of a heterogeneous surface, have been applied to the electrochemical determination of grain boundary corrosion^{60, 63, 64, 66, 68}.

Cihal and Prazak⁶⁰ determined the resistance of 18/8 stainless steel to this type of corrosion. They claimed that the technique could be used on steels which are difficult to test by other methods, including steels of low carbon content, and steels in which stabilising elements are present. By means of potentiostatic curves and light etching at constant potential they confirmed that the extent of intergranular corrosion depended upon the amount of precipitated chromium carbide.

Corradi and Gasperini⁶¹ claimed that the potentiostatic method was more effective and simpler than the Strauss test for determining intergranular corrosion of stainless steels, and suggested that the method may lend itself for use on finished equipment in service as a 'non-destructive' test.

Cihal, *et al.*⁶² tabulated potentials which may be used for the selective etching of the various phases in several stainless steels. Bergholtz⁶⁷ suggested a potential of +0.160 V vs. S.H.E. for grain-boundary etching of stainless steel, while Desestret^{64, 65} favoured various levels of potential, depending on its chromium content. He concluded that potentiostatic etching was more sensitive for determining susceptibility to intergranular corrosion than chemical tests in boiling nitric acid or acidified copper sulphate.

Budd and Booth⁶⁸ found the potentiostatic test best for investigating the intergranular and layer corrosion of aluminium alloys.

Not all test methods are necessarily accelerated by the use of a potentiostat. France and Greene^{69a} used a potentiostat to hold sensitised 18/8 stainless steels at various constant potentials in 1 N H₂SO₄ in order to determine the range of potentials at which intergranular attack occurred (see Section 19.1, Fig. 19.19). However, this method of testing for sensitivity has been criticised by Streicher^{69b}, who points out that the duration of the potentiostatic test is too short, and that alloys found to be immune during this test will suffer intergranular attack when the duration of exposure is more prolonged.

Streicher's work⁶⁹ indicates how useful the potentiostat has been in studying intergranular corrosion. Ideally, future data would be expanded to provide Pourbaix-type diagrams that also contain kinetic information showing various rates of attack within the general domain of intergranular corrosion. (Similar data for cases other than intergranular attack would be equally valuable.)

Stress-corrosion Cracking (s.c.c.)

S.C.C. has received a share of the potentiostatic approach to corrosion. Barnartt and van Rooyen⁷⁰ reported that potentiostatically controlled corrosion in a potential range 50–100 mV above the corrosion potential provided an accelerated test for the s.c.c. of stainless steels. The elevation of the potential by means of a potentiostat eliminated the incubation period, and also increased the density of cracks. Booth and Tucker⁷¹ used potentiostatic methods in the s.c.c. of Al-Mg alloys.

Hoar and his co-workers^{72,73} at first used galvanostatic equipment in their investigations into the 'mechano-chemical' dissolution of metal during plastic deformation; subsequently, the potentiostatic rather than galvanostatic control of potential was reported to give better results, and it enabled them to show that high corrosion rates were possible without appreciable elevation of the driving potential. This mechano-chemical theory has recently been refined in work reported for copper-base alloys^{74,75}. In the latter case, the potential dependence of the reactions leading to cracking has been analysed very carefully as a function of pH⁷⁶.

Staehle, *et al.*⁷⁷ have considered several aspects of s.c.c. from the electrochemical standpoint, including a feature of a recently suggested cracking mechanism which relates to the amount of corrosion that takes place each time that a slip step emerges at a surface. They recorded the shape of the current rise and decay curve that accompanied instantaneous straining (impact load), while the potential was controlled with a potentiostat. The number of coulombs of charge indicated the magnitude of metal dissolution. They believe that s.c.c. would be likely in a metal that showed the right amount of corrosion per slip step event.

Another contribution of the potentiostatic technique to s.c.c. studies has been the report⁷⁸ that cracking prevails essentially at two potential levels for metals showing an active-passive transition. These potentials are located near the top and bottom of the passive region. Along the same lines, Uhlig and his co-workers have determined critical ranges of potential for s.c.c.^{79,80}, although their theoretical interpretation differs from that of the other references cited.

High-temperature Water

Pressurised water nuclear reactors require metals that will have a high degree of corrosion resistance to pure water at around 300°C. Laboratory testing of materials for this application have included potentiostatic polarisation experiments designed to clarify the active-passive behaviour of alloys as well as to establish corrosion rates. Since pressure vessels are used for this work, it is necessary to provide sealed insulated leads through the autoclave head⁸³.

Care should be taken to avoid short circuits; for instance, an insulated specimen, being common with the ground point of some potentiostats, can become electrically reconnected to the autoclave if the latter is not separated from ground by using an isolation transformer.

Not all reference electrodes are suitable for use at high temperatures, and in addition, they may cause contamination if placed directly in pure water. A liquid junction consisting of a pressure-reducing tube with a wet string (or plug) has been employed^{81,84}; this enabled locating a reference electrode at room temperature and low pressure outside the autoclave, but compensation for contact and other potentials was difficult. Platinum has been used directly in the high-temperature electrolyte^{85,86}, and it functioned as a hydrogen electrode as long as hydrogen was present. Most recently, a canned electrode has been described⁸⁷, in which a silver-silver chloride reference is used inside a small container suspended in the hot water. Tiny pinholes and a long diffusion distance permitted a continuous electrolyte path while avoiding contamination of the test medium with chloride.

A review article on techniques for electrochemical measurements in pressurised water has been written by Jones and Masterson⁸⁸, which describes many of the experimental ramifications involved.

The low conductivity of high-purity water makes it difficult to study electrode processes potentiostatically, since too high an electrical resistance in the circuit can affect the proper functioning of a potentiostat, and it can also introduce large iR errors. The increase in conductivity of water with temperature has been measured⁸⁹ and iR -corrected polarisation data have been obtained⁸⁶ in hot water that originally had very low conductivity at room temperature. Other results^{31,83,85,90,91} in high-temperature water are all for tests where the conductivity was deliberately increased through the addition of electrolytes.

The interpretation of the polarisation curves requires care. Wilde⁸⁹ determined corrosion rates by linear polarisation in pure degassed water. Indig and Groot⁹⁰, however, found that electrochemical methods were unsuccessful in measuring the corrosion rate of Ni-Cr-Fe alloy 600 in the presence of hydrogen, owing to the kinetic ease of the redox reaction on the metal surface. In another paper, the same authors⁸⁵ also indicated that linear polarisation generally gave corrosion rates that were not accurate, as a result of competing half-reactions, under conditions that were different from those used by Wilde. In a test with stainless steel they found that the removal of hydrogen could reduce the problems.

Corrosion products are another source of error in the potentiostatic determination of polarisation curves in high-temperature water. In stagnant tests Fe^{2+} could be converted to Fe_2O_3 ³¹, causing a false anodic current

reading in the passive region. This effect was eliminated by using a flowing electrolyte.

S.C.C. has been examined as a function of potential⁸² in high-temperature water with chlorides present and an increased susceptibility of stainless alloys to intergranular attack was found as the potential was increased. Additional work⁹¹ reported that no intergranular cracking was observed in tests of short duration.

Hydrogen Permeation

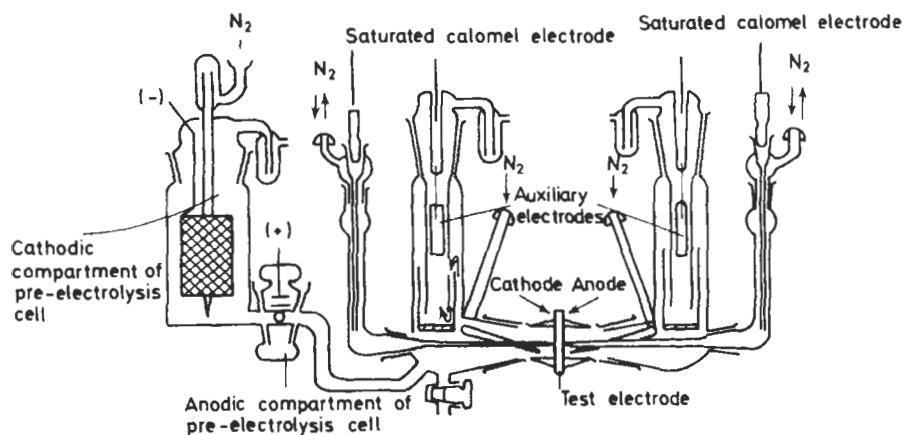


Fig. 19.45 Apparatus for studying the permeation of hydrogen through thin metal foils

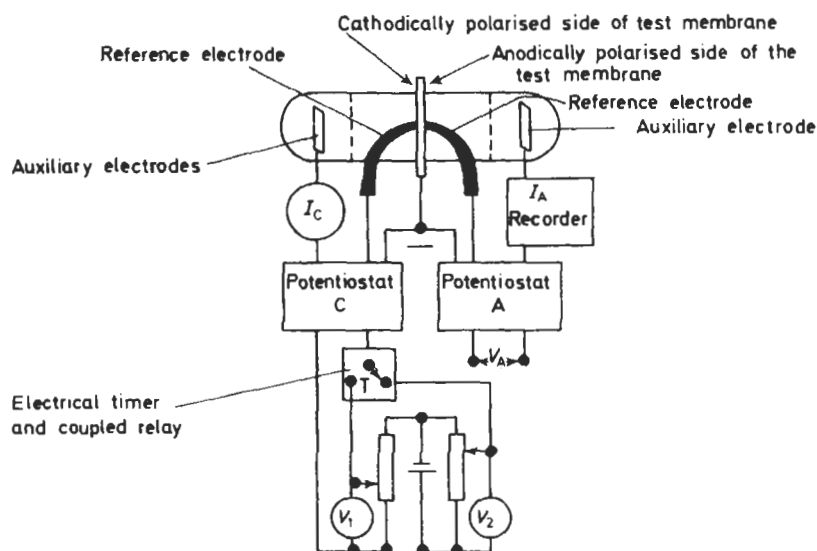


Fig. 19.46 Electrical circuit of cell and pre-electrolysis vessel (after Devanathan and Stachewski⁹³)

A very sensitive technique using the potentiostat was developed at the University of Pennsylvania⁹² for studying the permeation of hydrogen through thin metal foils. Such studies have and will continue to contribute important information in areas where hydrogen embrittlement is a problem. The technique involves the use of a double cell coupled by a thin metal membrane. Hydrogen is generated on the input side of the membrane which is maintained at a cathodic potential. Upon diffusion through the membrane, the hydrogen is electrochemically oxidised at the exit surface by an anodic potential that must be maintained constant by a potentiostat, and the anodic current provides a direct measure of the hydrogen flux. The technique is capable of detecting fluxes of $3 \times 10^{-2} \text{ cm}^3$ of H_2 per second and can provide information on diffusivity, permeability, solubility and the interaction of hydrogen with metallic lattices. The apparatus is shown in Figs. 19.45 and 19.46⁹³ and further details of the underlying theory are given in Section 20.1.

Molten Salts

The potentiostatic technique has been used in the investigation of the behaviour of metals in molten salts. In principle, the experimental method is the same as the one for aqueous media. Results are also capable of interpretation in the same way as those in aqueous solutions, and typical active-passive behaviour as well as anodic and cathodic Tafel lines have been observed. Reference 94 also contains several references to earlier work. These authors state that 'the potentiodynamic method, so successful in evaluating corrosion-resistant materials for aqueous systems, appears to be quite suitable also in selecting materials to be employed in molten salts'. In addition to the plotting of individual polarisation curves, it is possible to construct stability diagrams for molten salt systems resembling the well-known Pourbaix diagrams. The main difference is that the oxygen anion potential $p\text{O}^{2-}$ replaces the pH function, since the former is more important in molten salts.

It has been established that salts can deposit or form on metals during gas-metal reactions. Molten layers could then develop at high operating temperatures. Consequently, the laboratory testing of corrosion resistance in molten salts could yield valuable results for evaluating resistance to some high-temperature gaseous environments.

Inhibitors

There are many published papers dealing with the electrochemical investigation of the effects of inhibitors and surfactants on corrosion processes, using the potentiostat^{95,96}. Adsorption of organic and inorganic ions on metal surfaces is found to be important, since it is related to their positive or negative charges as well as the potential of the metal surface. Some details regarding the use of polarisation techniques for examining specific effects on anode and cathode kinetics are described in References 95 and 96; the reader will find that numerous other papers are also available.

Rotating Disc-ring Electrodes

Frumkin and Nekrasov⁹⁷ introduced a rotating disc-ring electrode suitable for the detection of intermediates in corrosion reactions, and its theory was considered by Ivanov and Levich⁹⁸. In this method, a disc electrode (specimen) can be corroded under controlled conditions, and a metal ring around it is held potentiostatically at a predetermined potential E_r in order to measure the rate at which an ionic species arrives at its surface; this is proportional to the current flowing in the potentiostat circuit. E_r is varied to appropriate values for particular ions of interest. Figures 19.47 and 19.48 are taken from the work of Pickering and Wagner⁹⁹, who applied the technique in their study of the de-alloying phenomenon. Modifications used by other workers include the 'split-ring' technique.

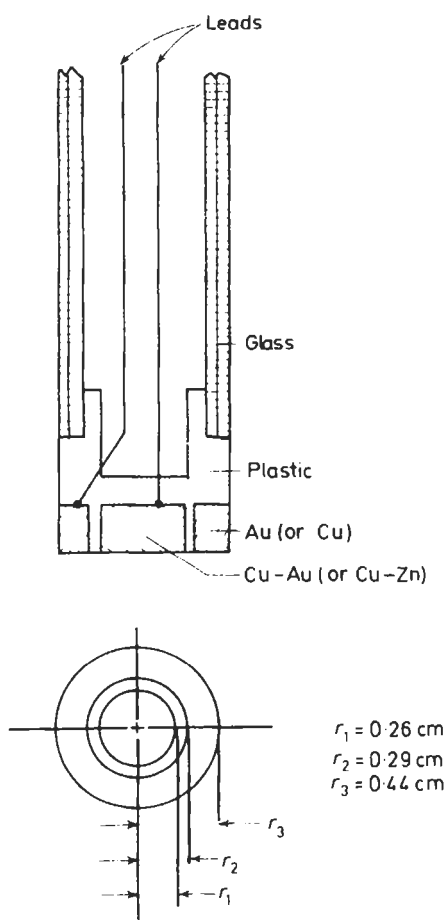


Fig. 19.47 Disc-ring electrode assembly

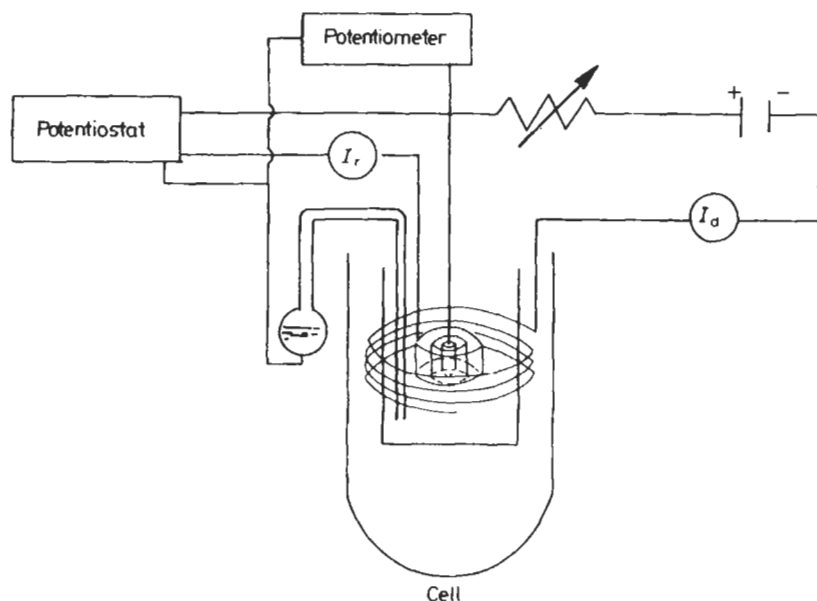


Fig. 19.48 Circuit used for the ionisation and redeposition experiments

Anodic Protection

The potentiostat has supplied an experimental tool for the study of anodic protection. The elucidation of passive behaviour made possible by potentiostatic anode polarisation curves allowed investigators to determine the conditions necessary for maintaining a metal in a stable passive condition by provision of a suitable environment, addition of cathodic alloying elements^{100, 101}, and/or maintenance of the required potential by means of external anodic polarisation^{27, 29, 106}.

Edeleanu^{102, 103} made use of potentiostatic curves to determine the optimum conditions for the protection of stainless steel in sulphuric acid. A pilot plant was then used to determine the practicability of anodic protection at a constant potential. He pointed out several factors necessary for proper control and indicated the spectacular results obtained.

Stern, *et al.*²⁹ obtained potentiostatic polarisation curves for titanium alloys in various solutions of sulphuric acid and showed that the mixed potentials of titanium-noble metal alloys are more positive than the critical potential for the passivity of titanium. This explains the basis for the beneficial effects of small amounts of noble metals on the corrosion resistance of titanium in reducing-type acids. Hoar's review of the work on the effect of noble metals on including anodic protection should also be consulted¹⁰⁴.

The use of potentiostatic curves has also facilitated the study of the rôle of oxidising agents and inhibitors in corrosion processes. Stern¹⁰ discussed the rôle of passivating-type inhibitors and used potentiostatic curves to explain their action. Posey¹⁰⁶ used the potentiostatic technique for determining the reduction of cupric ion on stainless steel. Both of these references

should be consulted for an extensive bibliography on these subjects. The reader will also find many subsequent papers dealing with this subject, and they generally confirm the principles that were set out in the aforementioned work.

Fast Electrode Reactions

Cahan, Nagy and Genshaw¹⁰⁷ examine design criteria for an electrochemical measuring system to be used for potentiostatic transient investigation of fast electrode reactions. They emphasise the importance of co-design of the experimental cell and electronics.

Accurate control of potential, stability, frequency response and uniform current distribution required the following: low resistance of the cell and reference electrode; small stray capacitances; small working electrode area; small solution resistance between specimen and point at which potential is measured; and a symmetrical electrode arrangement. Their design appears to have eliminated the need for the usual Luggin capillary probe.

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19.3 Corrosion Monitoring and Inspection

Introduction

The previous edition of *Corrosion* indicated an increased emphasis in monitoring of internal corrosion in high capital-cost process plant in the decade prior to 1976¹. A number of reasons for this were given; for example the requirement for process plant to operate for longer periods between scheduled shut-downs, avoidance of unscheduled stoppages, increased management efficiency and reduction in incidents resulting in hazard or injury to both plant personnel and the general public. These requirements particularly applied to oil and gas production as well as production of chemicals and petrochemicals.

Since 1976, all these factors have intensified, and reactions to political e.g. the OPEC crisis, which led to considerable expansion in the European off-shore sectors, which would otherwise have evolved more slowly. Also, during this time a number of events have led to greater awareness of the benefits to be obtained from on-line inspection to gain, in particular, information on the corrosion conditions of the interior of plant, pipework and pipelines. An example was the destructive explosion at the chemical plant at Flixborough (UK). Although the cause was not directly attributable to corrosion *per se*, the event catalysed mandatory requirements for overall inspection relating to the operation of process plant. In addition, industry in general has been undergoing a massive reduction in the workforce at all levels of responsibility—inspection departments were not exempted. It was inevitable therefore, for management to exercise interest in automatic systems for both corrosion monitoring and inspection.

The trend to automatic systems was considerably assisted by developments in computer technology especially the introduction of the micro-processor. Exploratory work regarding computer storage of corrosion monitoring data was reported in the last edition¹. Since that time rapid progress has been made in computer involvement in both monitoring and inspection techniques. Details will be found under the respective techniques. 'Closing the loop' where a computer can control and provide a remedy for up to 80% of corrosion 'alerts' arising from on-line monitoring is already operating in a number of oil refineries.

A factor which previously limited installation of automatic corrosion monitoring systems was the cost of cabling between sensors and control room instrumentation—this was particularly relevant to the electrical resistance (ER) systems. Developments to overcome this have included transmitter units at the probe location providing the standard 4–20 mA output (allowing use of standard cable) for onward transmission to data systems or the use of radio linkage which has been successfully used for other process-plant instrumentation.

Industry in general requires user-friendly equipment for industrial monitoring without the need for expertise for operation and data interpretation. Equipment and techniques that do require corrosion expertise will therefore, be limited to a 'service', i.e. specialist, company providing both equipment and personnel on a contract basis.

In addition to the general range of monitoring equipment, a number of instruments have been developed for detection and measurement of corrosion for specific requirements. Examples are the 'wheeled-trolley' using eddy currents for assessment of galvanised coating deterioration of high-tension transmission cables (Fig. 19.49) an electrochemical monitor for high-tension electricity cable pylons, a device for atmospheric monitoring (Fig. 19.50) and the use of thin-layer activation (TLA) for a subsea assembly used in oil production.

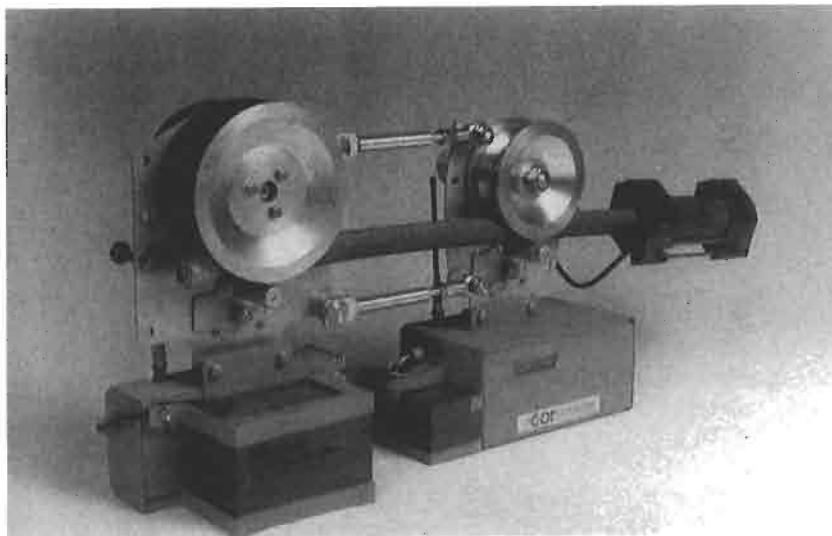


Fig. 19.49 Overhead line corrosion detector (courtesy Cormon Ltd.)

Developments in electrochemical methods since 1976 for measurement of corrosion have been rapid. Research and development has produced several new techniques, e.g. a.c. impedance and electrochemical noise. These methods require corrosion expertise for both operation and interpretation. Industry generally prefers instrumentation that can be operated by process

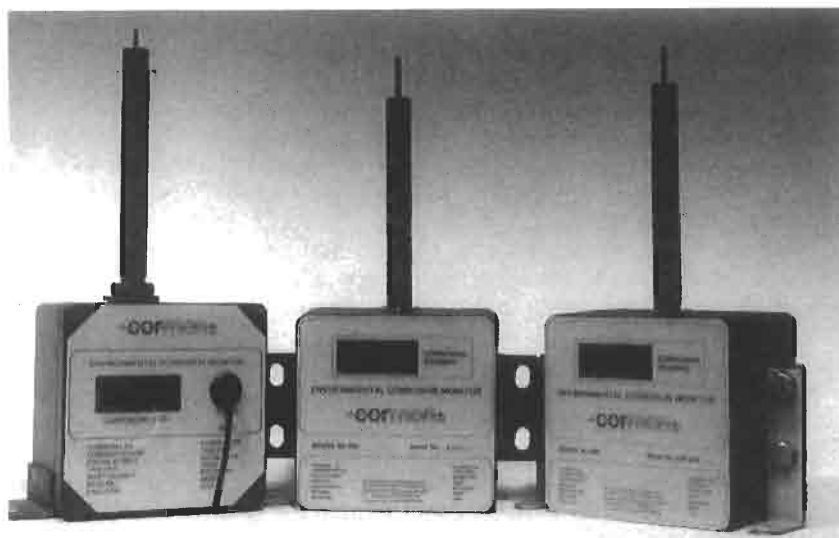


Fig. 19.50 Environmental corrosion monitor (courtesy Cormon Ltd.)

workers, so it is unlikely that such instrumentation systems will be sold 'over the counter', but will be supplied as a service to industry, as are the many advanced non-destructive testing (NDT) systems.

A considerable catalyst to the corrosion monitoring market has been expansion in the production of oil and gas, not only in the usual oil areas (US and the Middle East), but also the offshore developments in Europe. In addition to the usual uncertainty of the onset or progress of internal corrosion in the operation of plant, the oil industry has to face the considerable problem concerning prediction of 'field corrosivity' and the possibility of the producing field becoming corrosive or more corrosive as depletion progresses. These factors have considerable influence on the installation of corrosion monitoring as oil and gas production is the major user of such equipment.

It should be noted that there are still many deficiencies in the science and technology of corrosion monitoring, mainly in the areas of localised corrosion (pitting) and the inability to monitor at inaccessible sites such as 'downhole' (oil and gas wells) and subsea installations (satellite wells and pipelines).

Other problems (and successes) experienced by users of equipment are outlined in surveys (1981 and 1984) which present a broad spectrum of industry applications². The industries surveyed are shown in Table 19.6 and summaries of the findings of these surveys are shown in Tables 19.7 and 19.8. It is interesting to note that some of the problems highlighted in the 1981 survey had been considerably improved by the time of the 1984 survey.

Plant designers are well supplied with corrosion data by materials manufacturers. These data are based on both experience and laboratory studies, but the information is usually based on specific parameters such as concentration of chemical or temperature. Edeleanu³ has emphasised this problem

Table 19.6 Response rate by industrial sectors in the 1981 corrosion monitoring survey

	<i>Response</i>	
Oil and gas production	8/22	36%
Oil treating	6/20	30%
Chemical/petrochemical	9/11 (5/50)*	82%
Industrial boiler plants (excluding CEGB)	2/4	50%
Industrial cooling water systems	2/10	20%
Gas distribution	0/5	—
Electricity generation	3/7	43%
Pipelines	0/1	—
Mining	2/5	40%
Process plant contractors	1/5	20%
Miscellaneous	5/20	25%
Total	38 responses total	35%

* Five additional responses from a blind survey of 50 companies.

Table 19.7 Summary of the findings of the 1981 corrosion monitoring survey

Varied response
Widespread concern with the significance of the results and their interpretation
Ruggedness and reliability problems with equipment
Concern with intrinsic safety of equipment
Where corrosion monitoring is successful, several techniques are almost always in use
Widespread interest in new techniques
Universal use of NDT (especially ultrasonics and radiography)

Table 19.8 Summary of the findings of the 1984 corrosion monitoring survey

Increased awareness of the need for corrosion monitoring requirements to be considered at the plant design stage
Expanded use of corrosion monitoring in many companies
Greater appreciation of the qualitative nature of corrosion monitoring data and the need to learn by experience
Improved reliability of equipment, but much still to be done
Maintenance costs often too high
Desire to go more automatic and on-line
Awareness that system installation is expensive
Continuing interest in new techniques

with regard to stainless steel corrosion in sulphuric acid. Although the designer may select the correct choice of steel, it is certain that many times in the life of the plant, changes in concentration and/or temperature (as well as other parameters) will occur with a consequent increase in the corrosion rate above that anticipated.

Considerable corrosion monitoring is carried out utilising invasive methods, i.e. where the corrosion sensor is required to penetrate the pipe or vessel wall. Avoidance of penetration using non-invasive methods (thin layer activation, ultrasonics, radiography and magnetic fingerprinting) is receiving considerable developmental attention.

No one method for corrosion inspection is sufficient in itself and it is extremely dangerous to rely on data provided by one method only. A study is required of all methods available and the most suitable then chosen—

usually two or three methods are necessary. These are then used and additional methods can be called upon to supplement data if excessive corrosion is experienced or requires verification. This principle, outlined in the previous edition of *Corrosion*¹, was confirmed in the results of the surveys described above, i.e. an integrated system for corrosion monitoring and inspection achieved most of the objectives required².

Since 1976, two conferences have been held in London solely addressed to corrosion monitoring (*see Bibliography*). In addition, the main annual conferences devoted to corrosion in the US and UK, sponsor sessions in corrosion monitoring and the conference proceedings should be consulted for additional information. Also the NACE* and I Corr† Technical Committees have produced Guidance and Recommended Practices relating to various aspects of corrosion monitoring (*see Bibliography*; also details in text). Several publications and composite articles describing general aspects of the subject have been published since 1976⁴⁻⁹.

Several economic benefits arising from the use of corrosion monitoring have been published. An example of the savings that can be achieved relates to an offshore oil-field in the Norwegian sector¹⁰. Carbon dioxide corrosion problems necessitated a chemical inhibitor programme combined with the installation of automatic corrosion monitoring (cost \$1.2 million). The number of workovers (repairs to an oil-well), was reduced from twelve (1981) to one (1983). Each workover cost an average of \$2 million. This confirms the savings resulting from corrosion monitoring indicated previously¹.

Variables Affecting Corrosion Monitoring

The shortcomings of plant testing are considerable. Variables that affect the rate and type of corrosion are chemical composition, temperature, pressure, trace compounds or contaminants, velocity, presence of insoluble metal compounds, presence of insoluble materials (either as abrasives or deposits), crevices, stress (both magnitude and type are important), interface effects, phase changes (vaporising or condensing), chemical composition of the metallurgical condition of the metal and galvanic effects¹¹. No single corrosion test can include all of these variables and the corrosion data obtained should only be considered in this context. Mechanical phenomena, localised corrosion and stress-corrosion cracking are some of the factors that cannot be assessed with accuracy. Some sensor systems are now available which can make provision for thermal conditions.

Selection of Inspection Points

The selection of inspection points is of paramount importance, and factors to be considered have been outlined by Abramchuk¹² as follows:

1. Abrupt changes in direction of flow such as elbows, tees, return bends and changes in pipe size which create turbulence or changes in velocity.

* National Association of Corrosion Engineers (USA).

† Institute of Corrosion (UK).

2. Presence of 'dead-ends', loops, crevices, obstructions or other conditions which may produce turbulent flow causing erosion or stagnant flow which will allow debris or corrosive media to accumulate and set up corrosion cells.
3. Junctions of dissimilar metals which might promote severe galvanic (bimetallic) action.
4. Stressed areas such as those at welds, rivets, threads or areas that undergo cyclic temperature or pressure changes.

Selection of inspection points therefore, should be based on a thorough knowledge of process conditions, materials of construction, geometry of the system, external factors and historical records. Some of these factors may not be present, for example, when new plant is commissioned. There is greater knowledge now available concerning hydromechanics of fluid flows which should be considered when installation is planned.

Oil and gas streams require additional consideration regarding the phase to be monitored, i.e. water or oil stream, which in turn, will depend on the objectives of the monitoring, i.e. metal loss and/or optimisation of corrosion inhibitor addition. Factors to be considered are:

- (a) Top, middle or bottom line monitoring?
- (b) Flow regimes existing in pipeline or vessel?
- (c) Presence of different phases?

Access, Fittings

ASTM G4 (latest revision) gives guidance for conducting plant corrosion tests, and in particular, for various methods for mounting specimens (coupons) in process plant. This standard evolved from ASTM* and NACE Technical Committees.

Monitoring devices can be installed via standard gate-valves but these are only suitable for low pressures.

Since the last edition of *Corrosion*¹, there has been a trend to mechanical insertion/retrieval devices for coupons and sensors. These devices can be operated at pressure (whilst plant is operating), and utilise access fittings (Fig. 19.51). The equipment can now be obtained from several manufacturers in USA and Europe. These systems are safer to operate compared with probes utilising pressure glands fitted to plant via gate-valves. Consideration should be given to adequate space surrounding an access fitting thus allowing easy operation of the retrieval tool. Access fittings can be used for a variety of sensing devices (coupons and electronic probes), and can also be used for corrosion inhibitor injection using a suitable 'quill' injection nozzle.

The exposure of sensors in a by-pass stream (which can be valved off), is an alternative way of collecting monitoring data although correlation is required between the main-stream and the by-pass. The use of a side-stream taken either side of a choke in the main-stream can provide a useful monitoring point. Traps where product streams can be condensed can offer alternative sampling systems.

* American Society for Testing Materials.

HOW THE PLUG IS REMOVED AND INSTALLED UNDER PRESSURE

1. Access Fitting in service, externals removed.
2. Service Valve installed, retriever goes in.
3. Retriever is attached to plug.
4. Retriever extended, plug past gate, valve closed.
5. Plug removed.

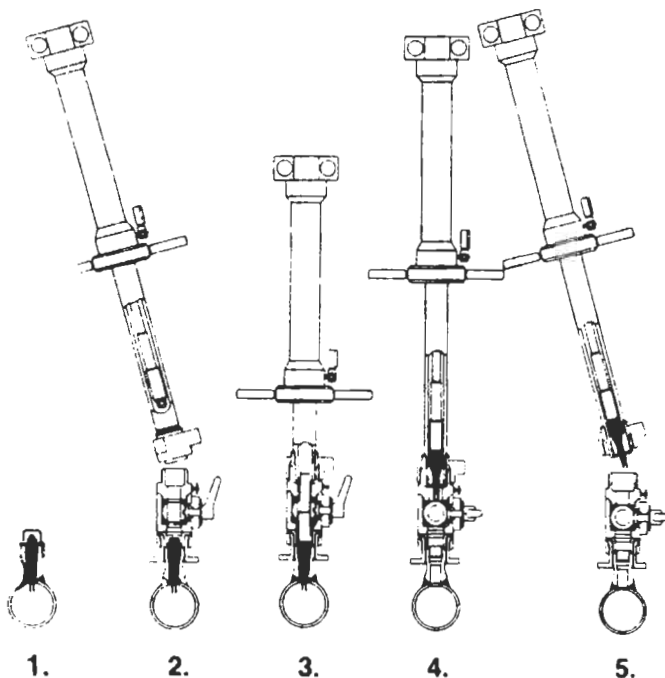


Fig. 19.51 Access fitting and retrieval tool (courtesy Rohrback-Cosasco Systems Ltd.)

Methods Available

Coupons These are usually strip, flush discs or cylindrical rods mounted in suitable racks (inserted and retrieved at shutdown), or installed in the plant using high-pressure access systems^{1,4-8}. Coupons are available from several manufacturers in a variety of materials and surface finishes and are supplied pre-weighed.

Comprehensive guidance for the preparation and installation of coupons is given by ASTM Method G4 (latest revision) and NACE Standard RP0775 (latest revision). Coupons can be heat-treated to represent plant material. It is important to anneal any stress arising from cold-work such as stamping or guillotining. Coupons can be welded for assessment of weld-corrosion and used to assess the possibility of crevice corrosion (using plastics or rubber bands). Photographic records provide valuable data as to the condition of coupons following exposure. Penetration of metal due to corrosion is calculated from the weight loss assessed gravimetrically.

Post-exposure techniques are well documented for a variety of metals (ASTM and NACE). A disadvantage of coupon techniques is that the response to severe corrosion that may occur for short periods of time is not detected because the response measured is only an average for the period of exposure, although coupons can be withdrawn at intervals of time provided a sufficient number are placed at the start of exposure. The important aspect of coupons is that data obtained from their use can be used as base-line and therefore can be used to correlate corrosion data from other methods.

Electrical Resistance Electrical resistance (ER), is the oldest electronic method for measuring corrosion following development for industrial monitoring in the US in the late 1940s^{1,4-8}. Guidance for using ER probes is given in NACE publication 3DI70. Most of the development was initiated by the oil industry. Instrumentation is now available from around six manufacturers in both Europe and the USA compared with only two in 1976.

A wire element (made of the metal of interest) is mounted in a suitable casing and exposed to the corrosive medium, which can be either liquid or gas. The element decreases in thickness due to corrosion and, as most corrosion products have greater electrical resistance than the metals from which

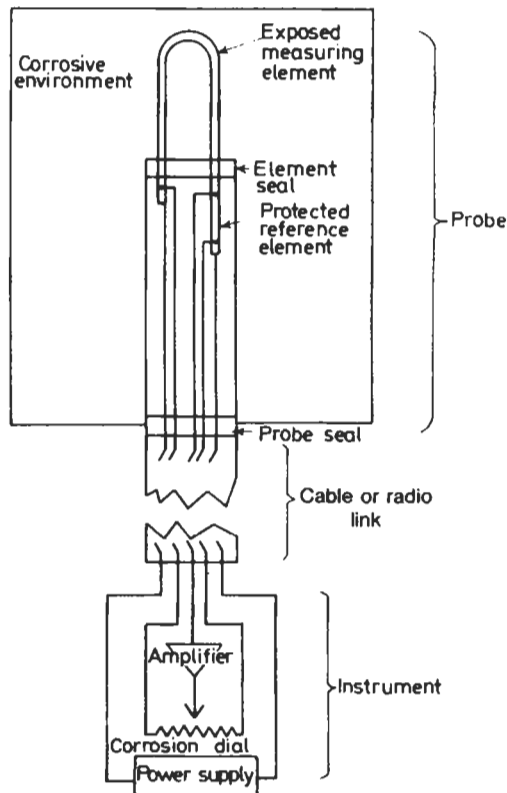


Fig. 19.52 Electrical resistance probe-circuit

they were formed, an accurate measurement of the increase in resistance can be equated with metal lost (Fig. 19.52). Temperature compensation for resistance changes is provided by reference elements mounted in the stem of the probe and protected from the corrosive environment.

A variety of elements in different geometric forms, e.g. wire, tube and strip, corresponding to the commercial metals and alloys used in the process plant, are available. Also a variety of casings or housings are available depending on temperature and pressure requirements (Figs 19.53 and 19.54).

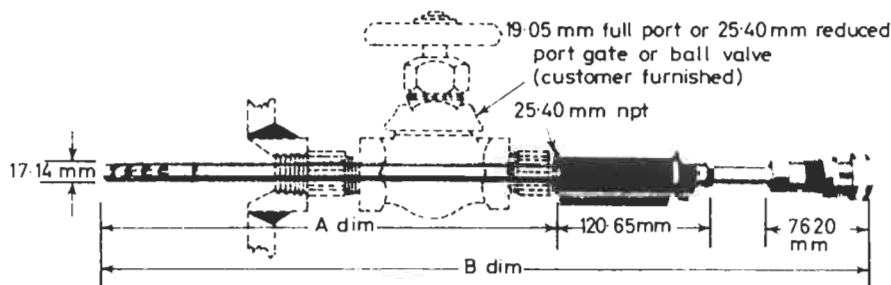


Fig. 19.53 Electrical resistance probe with screw-in fitting (courtesy Rohrback-Cosasco Systems Ltd.)

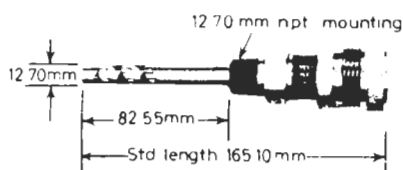


Fig. 19.54 Electrical resistance probe with retractable fitting (courtesy Rohrback-Cosasco Systems Ltd.)

Probes require insertion and removal from plant whilst the plant is operating and various methods for this are available (*see* section Access Fittings).

Consideration should be given to the compatibility with the corrosive environment of the probe casing materials as well as seals used in construction.

A complete range of instrumentation is available from portable units to automatic systems utilising many probes. Transmitter units are available which can be located at the probe and transmit ER data into the 4–20 mA standard instrument signal. Radio linkage from transmitter to control room or nearby offshore platform is available commercially. A satellite link has been used to monitor offshore platform ER probes at the onshore base¹⁰ in a Norwegian oilfield.

The data obtained from ER probes, and those provided by test coupons, are similar in giving an integrated or average rate, but the former has the advantage that the data are obtained whilst the plant is operating. The time periods can be decided by the frequency of measurement, and periods of

changing corrosion rate can be detected and measured whilst the plant is on-stream. It is usual to plot the probe reading against time, the slope of the line giving the corrosion rate at any particular time.

Pitting of the wire element increases the slope of the graph as the instrumentation cannot discriminate between general and localised attack. Pitting should be suspected if an increase in slope does occur and no changes have occurred in plant process conditions that would increase the general corrosion rate. Inspection of the element (another advantage in using retractable probes) can usually confirm whether pitting is occurring or not.

A 'flush' strip element is available for use in pipelines and obviates the necessity for withdrawal of probes prior to use of inspection vehicles. This element design more closely represents the inner wall of a pipe or pipeline.

The ER system has been used successfully in a range of industries for process plant monitoring. As ER can be applied in any liquid or gaseous environment the areas of application are considerable. However, there is a problem with ER if a conductive corrosion product is produced as is the case with sour crude oil or gas due to the deposition of iron sulphide.

Specific applications (apart from process plant monitoring) reported are:

- (a) atmospheric monitoring
- (b) assessing effectiveness of cathodic protection (connecting an ER probe to the structure being cathodically protected);
- (c) automobile body corrosion;
- (d) reinforcement corrosion (concrete);
- (e) marine piling;
- (f) aircraft

An ER probe specifically designed for assessing the effectiveness of cathodic protection is shown in Fig. 19.55. The elements for this probe can be machined from the actual pipeline.

Electrochemical Techniques

An overall assessment and guidance to electrochemical techniques has been published¹³.

Direct Current

Potential measurement This technique* has provided valuable information as to the condition of 'passive/active' materials, particularly in the chemical industry^{1,3-5,8}. Although quantitative weight loss measurements are not obtained, measurements can be on-line and more importantly, can be monitored using the actual plant material (*in situ*) as a sensor.

Choice of an appropriate reference electrode remains an enigma for 'non-corrosion-aware' personnel—although commercially available polarisation-resistance probes can be adapted. An interesting aspect concerns localised corrosion in that, for some materials, localised corrosion only occurs within characteristic potential ranges.

* Potential measurements concerning cathodic and anodic protection are excluded here.

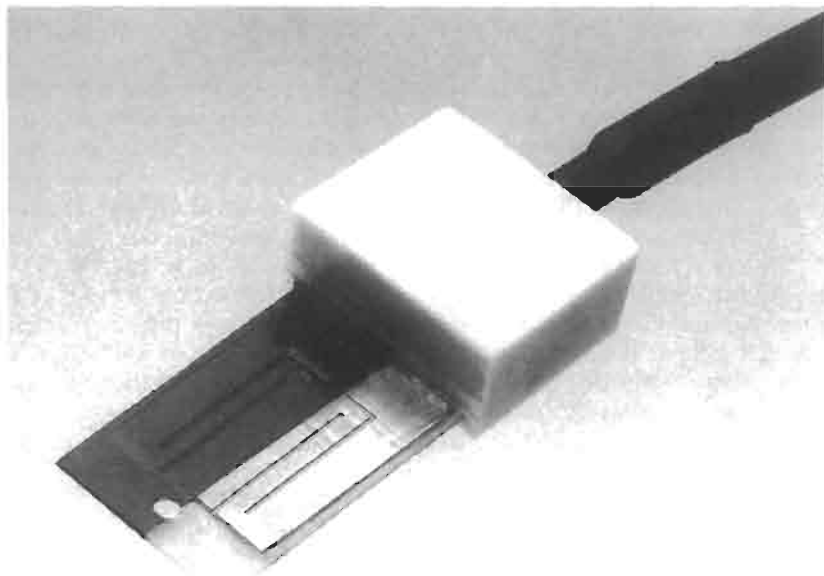


Fig. 19.55 Electrical resistance probe for assessment of cathodic protection (courtesy SSL Ltd.)

Potentiodynamic polarisation The characteristics of passive/active conditions for metals can be readily defined using this technique¹⁴. Details for laboratory application can be found in ASTM Standard G5 (latest revision). Application in plant is easily performed as portable equipment (potentiostat) is available from several manufacturers, with some models incorporating built-in computer facilities.

Tafel plots The linear part of the anodic or cathodic polarisation log-current and potential plot is extrapolated to intersect the corrosion potential line¹⁴. Low corrosion rates can be measured relatively quickly. Note that resultant oxide films may be of different composition from those occurring in practice owing to the several decades of current applied which may not relate to actual plant practice. Portable apparatus including computing facilities is commercially available for plant testing.

Polarisation resistance This technique, sometimes referred to as 'linear polarisation resistance' (LPR), has been applied widely in industrial monitoring because of its ability to react instantaneously to a corrosion situation or change in corrosion rate^{1, 4, 5, 8, 13-17}. The limitation of the technique arises from the necessity to have a defined electrolyte as the corrosive (the author has seen an LPR probe installed in a dry gas-line in an oil refinery).

The method applies a small potential (usually 10–30 mV) to a test electrode on either side of the corrosion potential (E_{corr}). The resultant current

is plotted against potential and the slope is used to calculate the corrosion rate. Aspects and errors arising from the use of two- or three-electrode probes (Figs 19.56 and 19.57) have been discussed previously¹⁸⁻²⁰. Recently there have been indications that modifications (by chemical treatment) to the probe dielectric (insulating the electrodes from one another) enable measurements to be made in less conducting solutions²¹. The process is thought to render the dielectric more conducting, minimising the *IR* drop which can be responsible for errors in using LPR.

Cyclic polarisation This type of measurement is similar to potentiodynamic anodic polarisation with the difference that, following an anodic polarisation plot, the test specimen is subjected to a cathodic stimulus, i.e. a reverse scan¹⁴. Any hysteresis, i.e. deviation from the anodic plot, can

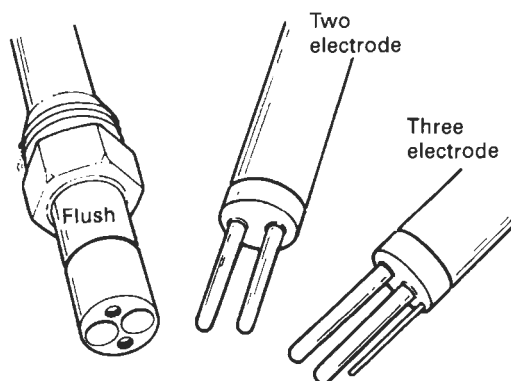


Fig. 19.56 Two- and three-electrode polarisation probes (courtesy Rohrback-Cosasco Systems Ltd.)

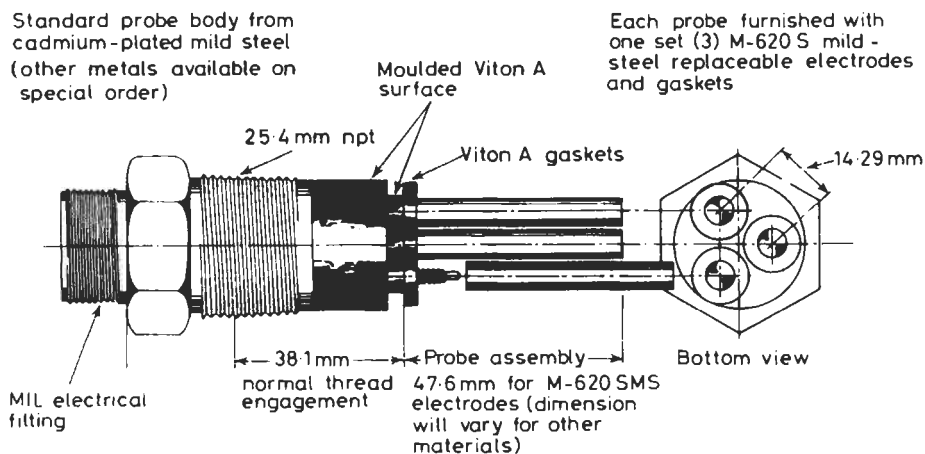


Fig. 19.57 Polarisation probe-three-electrode in screw-in fitting (courtesy Petrolite Corporation)

indicate a tendency for localised corrosion such as pitting. This method is widely used in the laboratory mainly for specifying corrosion properties of new alloys. With availability of portable potentiostats (plus computer data and plotting facilities), these measurements can be made *in situ* in process plant. Practices for carrying out these tests are given in ASTM G61. There is some controversy regarding this technique.

Galvanic current Measurement of the galvanic current between two different metals can be easily measured using a zero resistant ammeter^{1,4-8}. This method can have specific application, e.g. to provide a signal indicating failure of a protective coating in a process vessel. Commercial probes are available for industrial monitoring.

Measurements of current using 'same-metal' electrodes are utilised for electrochemical noise' measurements (see section below).

Alternating Current

Electrochemical noise This is a non-perturbation method and is defined as random low frequency low amplitude fluctuations either of the potential or current in a corroding system. Analysis of the corrosion potential noise can provide information relating to both the mechanism and kinetics of the corrosion occurring^{4,9,22,23}. The method has been applied to industrial monitoring in power generation plant, cooling water systems and reinforcement in concrete, and the method can provide information concerning localised corrosion and loss of passivity.

The corrosion process is observed as a series of events which all contribute to the overall corrosion rate. Measurement of rest potential fluctuations between two identical electrodes of potential fluctuations with respect to a fixed reference can be carried out. The electrochemical noise output spectrum is analysed using digitised data. The interpretation requires electrochemical expertise, and the method is therefore usually provided as a specialised service.

Development of this technique by CAPCIS (UMIST, Manchester, UK), has led to an instrument system utilising several electrochemical techniques (d.c. and a.c.) from a multi-element probe. Electrochemical noise was able to operate in an acid-condensing environment with small amounts of liquid²². The combination of data using several electrochemical techniques enabled identification of the corrosion mechanism in this application.

Impedance Some of the errors arising from the use of linear polarisation resistance led to interest and development in a.c. systems.^{4,9,13,24-26} An early development used a fixed a.c. frequency and a commercial instrument was produced in the UK. Inaccuracies still occurred, however, and were due to the electrode impedance which is frequency dependent. Electrode reactions have a capacitance component, in addition to resistance, resulting in a requirement to measure the impedance. However, the total impedance comprises values for the reaction, solution, diffusion and capacitance. Measurements at different frequency are more reliable, particularly where high solution resistances occur. Simplifications for industrial monitoring have been developed consisting of two measurements, i.e. at a high (10 kHz) and low frequency (0.1 Hz). The high-frequency measurement can identify the

electrolyte resistance and the other measurement relates to the corrosion process.

The advantage of the method is that measurements can be made in more resistive corrodents (crude oil and concrete) compared with linear polarisation measurements. However, corrosion expertise is required for both operation and interpretation, and most industrial applications, therefore, are provided as a specialised service.

The method is referred to as 'electrochemical impedance spectroscopy' (EIS), by Mansfield¹³.

Hydrogen

The hydrogen pressure-probe for detection of corrosion-produced hydrogen in industrial plant has been described^{1,4,5,27}. Since 1976, other manufacturers have produced equivalent versions of this probe type. Developments since 1976 have led to vacuum probes²⁸, and the 'patch pressure probe' where a saddle of steel is welded to the outside of the pipe or vessel and a suitable pressure gauge mounted in the saddle²⁹, thus avoiding penetration of the pipe wall. Electronic instrument systems are now available using a portable electrochemical cell that can be strapped to the pipe wall.³⁰⁻³¹ A solid electrolyte probe which overcomes problems arising from using corrosive acids (required as the electrolyte medium) is available³². These electronic probes work by oxidising hydrogen atoms on a fixed potential surface. All the above systems for monitoring the presence of hydrogen have given good performance in industrial applications. However, correlation with actual corrosion is not always easy and, at best, can only provide qualitative information. Guidance related to hydrogen probes is provided in NACE document ICI 84.

Thin Layer Activation

Thin layer activation (TLA) has a long experience in monitoring or measuring wear and erosion. A small quantity of radioisotope tracer is introduced into the metal surface which can be either a coupon or component. Metal loss due to corrosion (provided the corrosion product is non-adherent) can be detected remotely with high sensitivity^{2,8,33}.

A number of industrial applications have been described including successful subsea installation³⁴. Double layer activation has been used in the laboratory for estimation of both shape and growth of pits in stainless steel. Advantages of TLA are that (a) the concept is easily understood, (b) interpretation is relatively easy and (c) the system installation can be non-invasive.

Test Heat Exchangers

Test heat exchangers can be fitted to side-stream circuits in process plant which simulate actual temperatures existing in the plant³⁵. Condenser tubes can be removed and corrosion assessed.

Spool Pieces

Small lengths of piping (approx. 1 m in length) can be fitted to plant using appropriate flanges and can provide valuable data as to plant corrosion characteristics. The spool can only be removed at shut-down. An alternative procedure is to install the spool on a by-pass loop.

Chemical and Bacteriological Analysis

The contribution to corrosion monitoring by a well-planned chemical analysis programme is often underestimated. The most important analyses related to corrosion behaviour are: oxygen, hydrogen, trace elements, iron, manganese, corrosion inhibitor, other treating chemicals (biocides/oxygen scavenger), and pH. Guidelines for iron analysis (counts) in oil and gas production are given in NACE Standard T-IC-7 (latest revision).

Sampling points for analysis should be planned in order to give the whole record of analysis, e.g. in oil production from the well via processing facilities to the export facilities. Correlation with plant parameters such as temperatures, pressures, flow rates and, stream compositions can provide valuable records. Emphasis on chemical analysis should be incorporated in the design of process plant. Automatic analysis systems especially those using ion-sensitive electrodes with recording of data are recommended.

The initiation of corrosion due to bacteria is well recognised in a number of areas, in particular in oil production, the pulp and paper industry and municipal waste systems³⁶.

Testing for sulphate reducing bacteria (SRB) is expensive and time consuming, and considerable effort has been devoted to improve testing methods. Guidance for tests relating to oilfield practice are given in API* RP-38 and by the Institute of Corrosion. Methods of monitoring include bacterial analysis (via filters), side-streams and vessels and specially designed corrosion coupons^{37,38}. Rapid methods for assessing bacteria include ATP† photometry, fluorescence microscopy and radiorespirometry. However, these methods are not regarded as suitable for routine use³⁸. Commercial test kits are now available for sensing bacteria—a recent test developed by DuPont can be used for field testing and it is claimed that results can be obtained in 15 minutes³⁹. The Robbins device³⁷ comprises a 25 mm diameter pipe (stainless steel) with a series of carbon-steel studs—any sessile bacteria will deposit on the studs and can be quantitatively recovered and analysed. Variations of the Robbins device are commercially available for insertion into plant using standard access fittings.

Inspection

Visual Inspection and Mensuration This is regarded by Abramchuk¹² as so fundamental that it should be a logical prelude to most other inspection methods. A properly executed visual inspection can:

* American Petroleum Institute.

† ATP = Adenosine Triphosphate.

1. assist in failure analysis;
2. indicate the need for further exploration;
3. help to define the search area if further exploration is warranted;
4. aid in suggesting techniques for further exploration.
5. aid in determining the measures needed to prevent the recurrence of damage to equipment, or else minimise it;
6. reduce the possibility of installing faulty fabrications by ensuring that the right materials and procedures are used and that workmanship is of the proper quality.

Obvious signs of possible damage can include rust staining, bulging, cracked or distorted insulation, and hot-spots that are indicative of possible corrosion damage. The value of visual observation has been emphasised by Hobin⁴⁰ with a caveat concerning direct eye observation regarding access, fatigue and variability. Internal inspection can only be carried out when plant is shut down, but can determine the condition of many components.

The equipment utilised can range from simple types, such as callipers, pit gauges, scrapers, mirrors and magnifying glasses and endoscope systems, to complex equipment utilising miniaturised TV cameras and fibre optics. Description of devices used for inspection in the nuclear industry are described by Kovan⁴¹. Mechanical gauges (using spring-loaded feelers) for recording corrosion inside oil or gas well tubing have been marketed for many years. Although there are some disadvantages (restriction to off-line and damage to corrosion inhibitor films), much useful data can be obtained from these instruments.

Ultrasonics Use of ultrasonics involves the transmission of very high frequency sound waves through the metal whose thickness needs to be known^{1, 2, 4, 40, 42, 43}. An advantage of this technique is that access is only required to one side of the vessel or pipe wall (Fig. 19.58). A short burst of energy is transmitted via a transducer probe into the metal using the pulse-

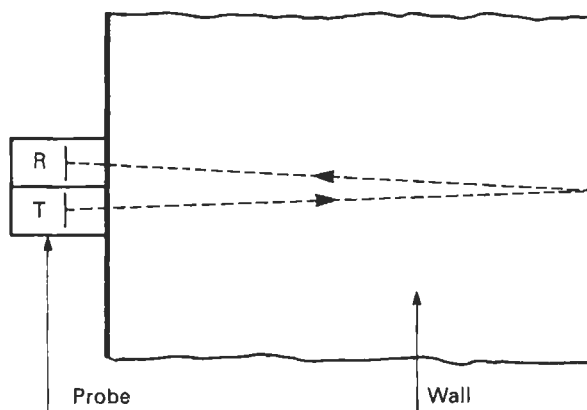


Fig. 19.58 Ultrasonic pulse-echo for estimation of wall thickness

echo system. The time taken for the sound to traverse the thickness of metal and return to the probe is usually displayed on an oscilloscope although digital read-out of metal-wall thickness is generally provided.

Modern thickness-gauging instruments are portable, measuring thicknesses from 1.0 to 300.0 mm to an accuracy of ± 0.1 mm⁴².

A problem associated with plant inspection is the coupling of the probe to the metal under examination. The exterior surface of plant can be covered in rust which causes problems in coupling the probe to the metal and results in spurious and inaccurate results. Often operators move the probe to an area where adequate coupling is obtained, circumventing the real objective of the measurement. It is often impossible to obtain any coupling on severely corroded steel surfaces, e.g. the interior of flash distillation plant chambers.

Temperature can destroy the piezoelectric properties of the probe, although techniques for cooling probes (delay blocks), and development of temperature-resistant piezoelectric materials, are extending the temperature range. Differences of up to 5% in thickness can occur between hot and cold readings.

Surface preparation before measurement is important, as sound travels about twice as fast in steel as in paint. Many years accumulation of paint can indicate a thicker steel wall than actually exists.

Pitting and other forms of localised corrosion are not detected easily, requiring complex equipment with separate probe assemblies for resolution of pits. Although there are shortcomings with corrosion measurement using ultrasonics, the contribution of the technique in an overall corrosion monitoring programme is considerable. This was confirmed in the surveys of users of equipment². The use of ultrasonics, combined with computer data handling and display has assisted not only in the inspection process but in overall record keeping.

The availability of the microprocessor has led to the development of multi-probe assemblies designed for specific applications, e.g. trolleys containing many probes used for inspection of oil-tank floors and sides of storage tanks and marine vessels. The incorporation of multiprobes in crawler-vehicles that can traverse vertical walls (oil storage tanks and ships hulls) can result in considerable savings, e.g. erection of scaffolding, compared with conventional hand monitoring.

Developments using ultrasonics related to corrosion detection have been 'zinscan' (digitally-based system with a scanning rig), and 'P-scan' (system incorporating a programmed scanning pattern using magnetic tape for storage and projection of images). The latter has been adapted for corrosion inspection of subsea pipelines. An ultrasonic probe has been developed for condenser tube inspection using a mirror to direct ultrasound to the tube wall from a probe that is passed through the tube. Inspection can only be carried out off-line.

The availability of probes that can be welded to the outer walls of piping or process vessels providing on-line thickness measurement is an interesting development which would seem to bridge the technologies of corrosion monitoring and inspection⁴⁴.

Ultrasonics has been utilised in several versions of pipeline inspection vehicle (see section below). The use of ultrasonics for detection of hydrogen damage in steels has been reported⁴⁵⁻⁴⁶.

The use of electromagnetic acoustic transducers (EMAT) obviates the coupling problems already referred to, and has been applied successfully to the inspection of boiler tubes. Ultrasonic time of flight diffraction (TOFD), developed by the Harwell Laboratory⁴⁷, is utilised to 'fingerprint' flaws (cracks) in process plant. Subsequent examination at, say, six month intervals can indicate any growth or extension of the crack. It is claimed that changes in crack height of 0.5 mm or less be estimated.

An overall assessment as to the reliability of inspection techniques (NDT), including ultrasonics, is given by Silk⁴⁸.

Radiography With its background of success in detecting weld defects and cracks, radiography (using X-rays or gamma-rays) can successfully reveal generalised and localised corrosion in plant^{1, 2, 4, 40, 42, 43}. Advantages are that pipe lagging need not be removed and permanent records are obtained which permit comparison with subsequent exposures. Several boiler tubes, for example, can be examined using one radiation source and spot checks can be made to units on-stream. Disadvantages are the radiation hazards, the time required to complete exposure, and the fact that access is required to both sides of the item to be examined.

Developments have included television fluoroscopy (allowing imaging in real time), X-ray tomography (using a computer programme to calculate and display an X-ray image absorbed in different directions) and flash radiography (short pulses of X-rays). Flash radiography has proved useful in detecting corrosion under pipe lagging⁴⁹.

Eddy currents The examination of non-ferrous tubing using external coils is a well-tryed and successful inspection technique, owing mainly to the pioneering work of Forster in Germany. The adoption of this method for *in-situ* inspection of condenser tubes, by mounting eddy-current coils in probes (or bobbins) that can be inserted in condenser tubes, was a logical development of the technique. Suitable apparatus was developed in the immediate post-war period more or less independently by several oil and chemical companies. The principle of operation has been described in the literature^{1, 4, 40, 42}.

In-situ inspection is concerned with corrosion in its many forms, such as pitting or more general attack and thinning. The double-coil probe, however, does not provide any output if general uniform thinning should occur in a length of tube exceeding the probe length. This can be overcome by winding a different coil or coil factor and the centre pole-piece may be moved to obtain a magnetic impedance between coils of equal numbers of turns.

Probes are available for a wide range of alloys and tube sizes, ranging from 6.3 mm diameter to around 50 mm diameter, which are suitable for tubes from 11.1 mm o.d. \times 1.8 mm wall thickness to 57 mm o.d. \times 1.6 mm wall. The probe is propelled through the tube by either winching or compressed air. Large and small holes, pits, larger areas of localised attack and cracks are easily detected. In addition, areas of selective attack such as intergranular corrosion or dezincification can be identified. An example of a tape recording artificial defects in a standard 25.4 mm o.d. \times 2.6 mm wall thickness (Type 316L) stainless steel tube is shown in Fig. 19.59.

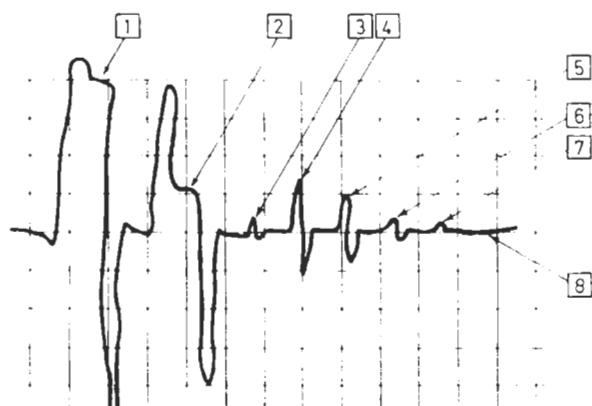


Fig. 19.59 Artificial defects in stainless steel tube

KEY

(1) 50% wall reduction. (2) 10% wall reduction. (3) Circumferential slot 0.254 mm wide \times 12.7 mm \times 50% gauge depth. (4) Longitudinal slot 0.254 mm wide \times 12.7 mm \times 50% gauge depth. (5) 1.59 mm diameter through hole. (6) 1.59 mm diameter hole to 50% gauge depth. (7) 0.78 mm diameter through hole. (8) 0.78 mm diameter hole to 50% gauge depth

Most eddy current equipment is custom designed for a particular application. Signals can be digitised allowing computer signal processing. Many materials can be tested, and they include copper, cupro-nickel alloys, brasses, stainless steels, zirconium, zircaloy, tungsten, molybdenum, lead, beryllium and titanium. It is usual to check the calibration of the instrument with a tube having calibrated defects. The baffles supporting the condenser tubes may mask any corrosion occurring close to the baffles.

Infrared Methods Commercial instrumentation for recording infrared radiation has been available for some years and has been explored by the electrical power industry in the UK for assessing corrosion in boiler tubes at power-station shut-down. An external heat source is played onto the outside of boiler tubes at the same time as cold water is circulated inside the tubes. Hot spots due to poor heat conductivity caused by excessive corrosion product indicated areas of high corrosion.

Acoustic Emission Acoustic emission (AE) describes the technique in which sound generated by a metal under stress can be detected^{4, 40, 42}. The method can provide indication of cracking or other defects in process equipment. Advantages of the technique are applicability to on-line monitoring (claims that cracking can be detected and arrested on-stream have been made) and that tests can be made relatively quickly. The equipment required has been described by Halmshaw⁴² who indicates the controversial claims for this technique. There is no doubt that successful applications of AE are now being reported for corrosion detection, in particular an application regarding stress corrosion cracking⁴². AE is provided as a service by specialist firms.

Magnetic saturation This method has been adopted for several versions of intelligent vehicle (instrumented devices that are propelled through pipelines to assess both internal and external corrosion, *see* section below). Magnetic flux exclusion (MFE) has been used for detecting pitting in oil storage tank floors by the Harwell Laboratory⁵⁰. The instrument specification required that reliable indication be given of any underfloor corrosion pit in carbon steel plate a diameter greater than that produced by a 120° cone penetrating 3 mm into 6 mm plate.

Intelligent Vehicles (for pipelines) The oil and gas industry has for a long time used devices which are passed through pipelines (propelled by the product being transported) for (a) cleaning the interior of pipelines and removal of paraffin waxes and (b) pipeline inspection using photographic, TV and mechanical gauging equipment^{1, 4, 51, 52}.

The consequences of high pressure pipeline failure can be catastrophic (occurrences have been recorded in both the USA and eastern Europe), and much effort has been devoted to the development of intelligent vehicles or PIG (PIG = pipeline inspection gauge) using various NDT techniques for inspection. A recording of data is made during a pipeline run, data within specification is discarded, and the tapes analysed at a base computer^{53, 54}. Reliability and confidence in those vehicles is continuously improving and they will be utilised to a greater extent in the future because of more stringent legislation being applied to pipeline operators in several countries. Factors to be considered are the products in the pipeline (gas/liquid), facilities for loading and retrieval of the vehicles (called pig-traps), condition of line prior to inspection (dents or damage that would prevent passage of the vehicle), economics and size of pipeline.

The British Gas version uses magnetic saturation, and can identify corrosion on both internal and external pipe surfaces. The specification for seamless pipe is:

	<i>Detection sensitivity</i>	<i>Sizing accuracy</i>
General corrosion	$0.2t$	$\pm 0.1t$
Pitting corrosion	$0.4t$	$\pm 0.1t$

where t = nominal pipe wall thickness (seam welded pipe), and pitting corrosion is defined as corrosion affecting a surface area of pipe contained within a square of dimensions $3t \times 3t$.

Intelligent vehicles have been developed with arrays of ultrasonic probes for pipeline inspection—one commercial version contains 512 ultrasonic sensors.

Under development are intelligent vehicles for crack detection. An elastic-wave version (developed by British Gas and the Harwell Laboratory) is currently being evaluated in a test-loop. This vehicle has successfully detected stress-corrosion cracks in the test-loop. The Gas Research Institute (USA) is sponsoring development work with intelligent vehicles at the Battelle Columbus Division (Ohio). Facilities for testing vehicles were commissioned in 1991⁵².

Industry Requirements, Philosophy and Case Histories

Oil and Gas Production This sector is a major user of corrosion monitoring equipment, in particular for offshore fields where ramifications of corrosion and consequent maintenance are far more serious and costly compared with onshore production. Carbon steel is used for approximately 70–80% of production facilities. The development of a field is assessed on a defined corrosion risk which may not be correct, leading to serious corrosion. In addition, a reservoir may become more corrosive as the field is extracted owing to (a) increased water content, and (b) eventual 'souring' of the field (hydrogen sulphide production).

As well as corrosion in oil and gas streams, there are other applications such as various water circuits and injection of treated sea-water into the reservoir.

The structures used (platforms) require monitoring in addition to sub-sea pipelines, satellite wells and other equipment (e.g. manifolds) on the sea floor. Corrosion inhibitors are widely used in internal-streams (from the reservoir and many of the downstream operations). Corrosion monitoring can provide valuable data for assessing the effectiveness of the inhibitors used and for optimising dosage rates.

User experience of monitoring techniques in oil and gas production has been reviewed⁵⁵ and indicates success and failure for the same methods by different operators. A survey of current monitoring practice in UK offshore fields has been published⁵⁶, and other experience related to oil/gas production has been reported^{57,58}. A draft document has been prepared by CEA Task Group E2-5 providing guidelines for monitoring sea-water injection systems.

Oil Refining Substantial corrosion monitoring is used in oil distillation and other refinery units. Refineries are major users of corrosion inhibitors depending on the processes and materials adopted. The utilities necessary for the refinery operation, e.g. steam and cooling water, also require monitoring. Miller⁵⁹ has provided a review of one particular company philosophy regarding corrosion monitoring in oil refining. Loushin⁶⁰ has outlined the benefits from computer application in the overall monitoring and inspection programme.

Chemical and Petrochemical Production One of the earliest applications for corrosion monitoring is in chemical and petrochemical production. In contrast to the oil industry, more exotic metallurgy is used requiring different monitoring data, e.g. monitoring of potential for stainless steel to indicate passivity or activity. Localised corrosion is a common mode of failure and still presents a challenge to monitoring technology. Chemical plants also have large requirements for utilities, e.g. steam and cooling water. Case histories in chemical plant monitoring have been published^{4,61–64}.

Boilers Plants always experience corrosion problems with boilers, and monitoring of corrosion has always presented a challenge relating to both access and simulation of exact conditions, e.g. condensation conditions. Applications in the monitoring of condenser tubes have been reported^{65–66}.

Industrial Cooling Water Systems Waters used for recirculating cooling systems can either be scaling or corrosive. Corrosive waters are treated with corrosion inhibitors which require monitoring for overall assessment of the treatment programme.

Pipelines Pipelines carrying wet gas and crude oil present a corrosion hazard and are protected accordingly by coatings and/or inhibitors. Limitations of corrosion monitoring arise from sampling, in relation to the sampling and interval, and access problems for subsea pipelines (major trunk lines).

The use of inspection by intelligent vehicles which are sent through pipelines is increasing but is still limited to inspection only with long intervals between each inspection (1–3 years). The performance of these intelligent vehicles is dependent on the type of vehicle utilised.

Civil Engineering The corrosion of concrete reinforcement (rebar) is a serious problem which is attracting much research effort. Solutions being examined include epoxy coatings, exotic metallurgy and/or adoption of cathodic protection. Monitoring and inspection is a major challenge in this area, as is the monitoring of the effectiveness of the chosen corrosion prevention method. Most major civil engineering structures may be affected. A review of techniques for monitoring corrosion of rebar in concrete has been published⁶⁷. A state of the art survey of possible methods for monitoring rebar in concrete concluded that electropotential measurements were the only practicable NDT aid to diagnosis of corrosion in the field⁶⁸.

Miscellaneous There are many interesting applications that arise from time to time that are outside the main stream of industry described above. Examples include: desalination plant; reactor cooling water circuits; automobile body corrosion (*in situ*); marine (vessels, piling, harbour installations); aircraft (*in situ*); packaging; and cavitation monitoring.

Future Developments

A thrust can be expected in development of the electrochemical methods (reliability, operation and interpretation), TLA and custom-built NDT systems for specific requirements. The disadvantage of using separate sensors rather than the actual plant has been stated. Methods that can use plant for data are required, and developments in magnetic finger-printing may contribute here.

The use of expert systems combined or in conjunction with corrosion monitoring and inspection techniques will provide an attractive synergistic approach to the control of corrosion in process plant in the future⁶⁹, providing the corrosion monitoring techniques used are reliable and sufficiently rugged for industrial use. The inability to monitor corrosion in inaccessible areas (oil/gas-well tubing) and for specific applications (corrosion under lagging) are examples of deficiencies in the overall technology.

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In addition to the above the annual corrosion conferences (NACE and UK Corrosion), usually sponsor sessions on corrosion monitoring which are reported in the respective proceedings.

The British Institute of Nondestructive Testing (Northampton) and the American Society of Nondestructive Testing (Ohio) publish transactions and sponsor conferences/symposia on a regular basis.

Standards and Recommended Practices relating to corrosion monitoring are published by both ASTM and NACE. The Institute of Corrosion (UK) publishes European practices and experience via the NACE Technical Committee system.

19.4 Inspection of Paints and Painting Operations

Improvements in process and quality control made significant contributions to the transition from iron to steel as the major ferrous construction material over a century and a half ago. For most of that time red lead was relied upon, and not without a remarkable degree of success, as the rust-inhibitive pigment in anti-corrosive paints. In the last twenty years, however, there has been a similar dramatic change from such simple paints as red lead to synthetic polymer coatings which have as complex a technology as steel manufacture itself.

Improved processes and quality control have helped to establish these new coating materials but the care necessary for successful use has to be appreciated. Sections 11.1 and 11.2 have shown how necessary it is to remove millscale before coating and how scale-free surfaces may still retain seeds of further corrosion even when apparently cleaned well. The percentage of premature failures with sophisticated systems is still high, even on apparently well-prepared surfaces and there is a strong case for effective inspection at each stage of coating operations.

Painting of Structural Steel

It is not always easy to apply the concepts of quality control which have become routine on coating production lines to single structures. For instance, in ordinary steelwork fabrication shops the service conditions for which a significant proportion of the throughput is required, simply do not call for high performance systems to be applied. This generally means at least two levels of quality in one works. The problem is further complicated by the multiplicity of techniques involved and the near-uniqueness of every steel design. Nevertheless, many conditions of environment, use, maintenance and safety, exist where it is essential to produce long-life protective coating for structural steel. Only by continuous inspection of surface preparation and coating application, however, can high performance from modern systems be achieved with certainty.

Case Histories and Cost

To illustrate the above, consider two case histories¹ where no specialist inspection was provided.

Figure 19.60 illustrates a steel surface which should have been blast cleaned to a high standard before being coated at works with a zinc-rich epoxy primer and on site with two-pack intermediate and finishing coats. After exposure for 18 months in a marine environment, flaking millscale from beneath the paint was observed, and a survey showed that the paint

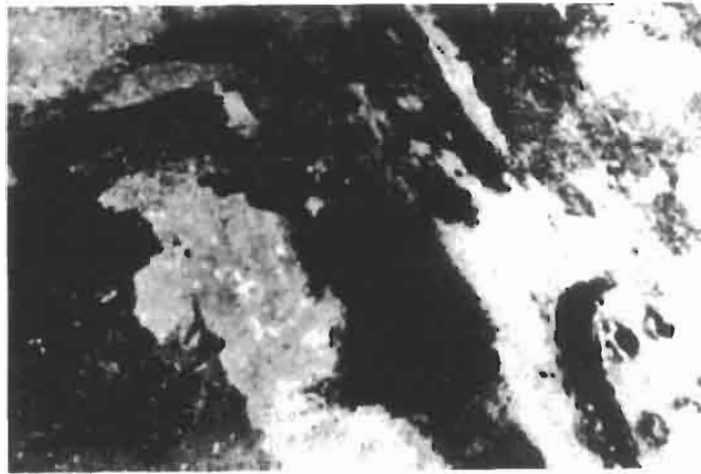


Fig. 19.60 Rusting surface after marine exposure for 18 months; no inspection during the coating process

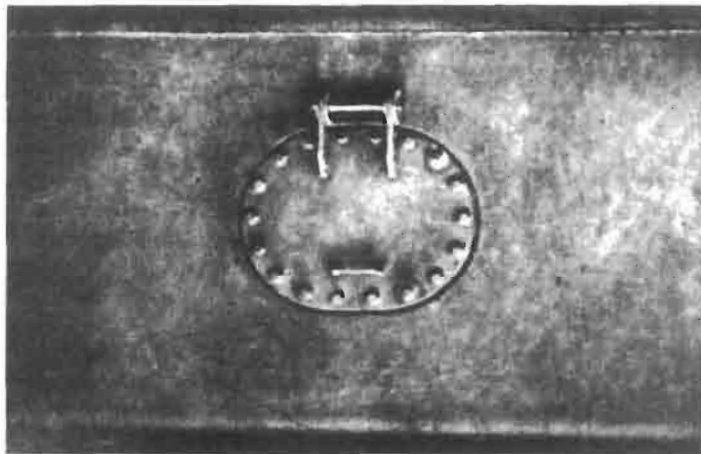


Fig. 19.61 Same section shown in Fig. 19.60 photographed 4 years after remedial work; full inspection during recoating on site

film thickness varied between 50 and 140 μm . Some parts had not been primed. Although the remedial re-blast cleaning of all surfaces had to be carried out *in-situ*, and a suitable system applied, the resulting protection (Fig. 19.61) after exposure for 4 years was still of the high order expected. The only difference between the two contracts was that full-time specialist inspection was given at every stage of the site remedial work.

Figures 19.62 and 19.63 were taken at the time of investigation into a failure of 100 t of steel which should have been coated with a nearly maintenance-free system. Zinc metal spray and four coats of paint were specified but, for reasons of economy, special measures for inspection were not taken. Within months of erection areas were flaking off where millscale had not been removed (Fig. 19.62) and other areas were blistering. Figure

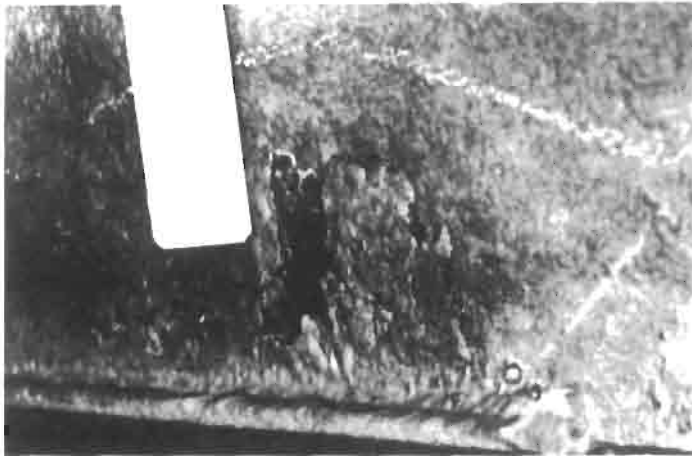


Fig. 19.62 Result of millscale not being removed from steelwork before zinc metal spraying

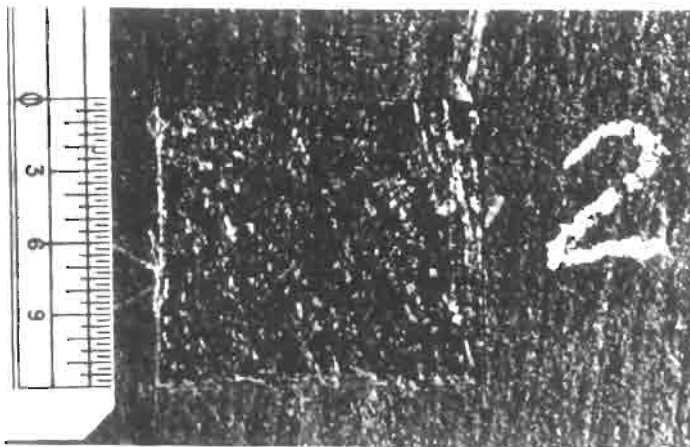


Fig. 19.63 Random check of the surface of the steelwork shown in Fig. 19.62 showing the surface completely oxidised under the coating

19.63 shows one of the many areas investigated where there were no visible signs of failure until the whole system was removed; the dark surface in the cut-out area represents the rusted metal found underneath the metal spray. Subsequent investigation revealed that the steel members had been too long to be housed completely in the workshops concerned. The blast-cleaned surface had been allowed to stand outside overnight and had been metal sprayed the following morning. No one had visited the works before the order had been placed to see if the contractor would be able to cope with this very long steelwork. The benefit of the protective system specified had been lost for good. The compensation finally paid could never recompense the owners fully as *in situ* repair was made very difficult by restricted access.

Prior Inspection of Works and Site Facilities

Before a works painting or metal spraying contract for steelwork is awarded, the workshops concerned should be inspected by qualified personnel. It is essential that some check is made to ensure that the necessary facilities and equipment for carrying out all the terms of the order or specification are available. Cleanliness of the painting areas and order in the paint store usually indicate the seriousness with which works personnel take protective-coating operations.

Prior inspection should also be made on site to ensure scaffolding and platforms have been erected to give the operators easy access to the work, i.e. at the correct level to, and distance from, the surface to be treated; temporary covers and equipment, including compressors, should be included in the survey.

The safety of operators, the rigging of life-lines for scaffolding, and the proper removal of dust and solvent vapours should be discussed with the management.

Type of Inspection

The British Standard Code of Practice for protecting iron and steelwork from corrosion, BS 5493:1977² contains a section on inspection which may be helpful. This type of inspection is entirely unnecessary for very simple painting schemes. In such situations an occasional visit by an inspector may be sufficient to ensure acceptable results once initial standards of surface preparation and paint application have been established.

For the many systems which may be specified today, some will require the maximum level of surface preparation and demand continuous inspection at every stage. Others will require less onerous policing. It is up to the client to determine the appropriate level of inspection for the job and to make financial provision for this.

Quality of Inspection

This will depend partly on the experience and personal integrity of the inspector and partly on the organisation to which he belongs. Whatever the type of inspection ordered, the inspector himself should always be experienced in the processes concerned.

The organisation behind the inspector must be sufficiently competent in coating technology to give him the backing he requires, to answer his queries by telephone if necessary to prevent delays (although anticipation is the hallmark of the competent organisation) and to provide consultants to investigate and report where necessary. Some of the larger owner organisations, e.g. government departments, public utilities and major contractors do have such staff but, where a long-life protective-coating contract is awarded, it is becoming more and more frequent for them to employ independent inspection firms who specialise in this field and can even provide teams of inspectors where necessary.

Independent Inspection Organisations

On its appointment to provide inspection for a coating contract, the organisation concerned might be expected to include in their service the following:

1. Constructive criticism of the coating specification, bringing to the attention of the client aspects that may be difficult to implement fully.
2. Initiation of preliminary discussions on the contractor's proposed methods of working.
3. Close liaison with the coating manufacturer on materials and their use.
4. An introductory schedule showing precisely how and at what stages inspection will be carried out and reported.

Inspection schedule It is not unusual for those who employ such firms to ask for an inspection schedule as suggested in (4) above, prior to making an appointment. Some large organisations lay down in general terms the numbers of inspectors and how they require the work to be inspected. However, the inspection schedule is not only the key to what may be expected from individual firms, it is also useful in summarising the inspector's duties and in informing the contractor as to how his work will be checked.

Preliminary Discussions

Preliminary discussions of all those involved in each protective-coating contract are essential if certain difficulties that can arise in these operations are to be prevented. Although the ultimate client may not wish to be present, the engineer concerned and/or his own or appointed inspectors, the main contractor, steel fabricator and coating contractor, should meet to discuss and agree action on such subjects as the following:

1. Ambiguities, inaccuracies or omissions in the coating specification.
2. Details of design which may impede or prevent the implementation of the specification, possible changes in design or alternative treatment for special areas.
3. The methods of inspection to be used; the instruments to be used and pass figures have to be agreed by trial beforehand.
4. The programme for all operations, bearing in mind pot-life, recoating intervals, approximate ageing before transport, etc.
5. Special measures to reduce coating damage during handling, transport or erection and measures for maintenance of incomplete systems stored in the open.
6. Arrangements and facilities for the testing of materials.
7. Manufacturers' data sheets.
8. Any special skills required for operating equipment.
9. The procedure and responsibility for 'stopping the job'.
10. The chain of authority with client and contractor, to be followed in cases of difficulty.

The minutes of such a meeting should be detailed enough to be agreed by all parties and serve as a rider to the contract.

Inspectors' Duties

Apart from his liaison, progressing and reporting duties, the inspector of protective-coating operations has three quite distinct areas of operation:

1. The materials to be used (which includes the substrate).
2. The surface preparation of the substrate.
3. The application of the coating or coatings.

Given below are the points to watch, the measurements to be taken and the standards for comparison, but it must be emphasised that they are for long-life systems only.

Materials

The supplies of the specified paint, blasting abrasive or other materials involved in the coating process should be checked to make sure that they are adequately stored and available in sufficient quantity to permit operations to begin. Sometimes it is part of the inspection contract to sample and check to a predetermined schedule in the laboratory that supplies are up to specification. It is always the inspector's duty to ensure to the best of his ability that material that he has checked in the stores is being used on his job (*see Sampling and Testing, later*), and that the information on the container labels agrees with the specification requirement. The basic substrate offered for treatment in the case of steel will normally be subjected to steelwork inspection, but the painting inspector has the duty to point out to the contractor for rectification any omissions that he may have noticed, e.g. that it should be free from pits, that it should be machined or that edges

should be radiused, that certain areas should be masked from any treatment, etc.

Additionally the inspector should ensure that the specified measures for removing oil and grease from the surface with water-rinsable solvent or emulsion cleaners are implemented, and that all weld-spatter and other asperities have been removed as a preliminary to surface preparation.

Surface Preparation

Certain British Standards, e.g. for galvanising³ or metal spraying⁴, contain detailed sections on surface preparation. Others are concerned with acid pickling but the chief method of preparing iron and steel for a long-life protective system is by blast cleaning (see Section 12.4).

The inspector's working standard for the surface finish of blast-cleaned steel is now the new British Standard⁵. In the special circumstances where absolute freedom from soluble contaminants such as ferrous sulphate is necessary, the specification should include reference to a test for removal of such residual salts, e.g. the potassium ferricyanide test⁶. The area to be sampled should be wetted with a fine spray of distilled water and the paper held against it. The development of blue spots on the paper indicates the presence of ferrous salts on the surface.

Methods are available for checking on the profile of blast cleaning which is of particular importance where a prefabrication or holding primer is used or where the total protective system has a limited margin of thickness over the profile height. Peaks far in excess of the normal profile (rogue peaks) may be produced by insufficiently controlled sweep of the blasting nozzle or by using an abrasive with excessive particle size, and the inspector has to be aware of this. On site, surface profile can best be measured with an ISO comparator⁷. Where profile is important the method of measurement should be stated in the specification and agreed at the preliminary discussions. A retained sample of the abrasive used in the process during the early trials for setting acceptance levels in the works can be used as a standard against which to make *ad hoc* checks later, or when prompted by high-profile measurements.

It frequently happens that after surface preparation 'shelling' or other imperfections in the steel surface are revealed. It is preferable to deal with these by grinding or filling as necessary before any other coating is applied.

Application of Coating

Paints have their own individual data sheets, prepared by the manufacturer as the result of extensive testing including laboratory tests, field trials and experience in use. These instructions should be followed closely in respect of type of application equipment, operating air pressure, tip size, pot life, curing time at various temperatures, recoating interval, etc. The inspector should have the data sheets available at all times and refer to them.

Holiday detection or 'spark testing' may be specified in the contract with details of the appropriate instrument and testing procedure. In certain cases,

where the conditions of service include exposure to chemicals or other hostile environments, the test is essential.

Thickness Measurements

In the case of a paint coating the film thickness may be determined when the film is dry or when it is still wet; both methods are described and discussed in detail in BS 5493², but some discussion is appropriate here.

However the paint film thickness is specified in the contract, it is an obvious advantage to all parties for the painter himself to have a means of checking whether or not he is applying sufficient paint, and this can be achieved for each coat by means of a wet film thickness gauge. The relationship between wet- and dry-film thickness can be provided by the paint manufacturer. Wet gauges must be used immediately the paint is applied if they are to give reliable results. Many non-destructive instruments are available for measurement of the dry-film thickness and in general these are to be preferred to the destructive methods, which may however be necessary for an official investigation or for agreed certifying tests. The main group of non-destructive instruments employ a magnetic principle. Many of them also contain an integral microprocessor to store readings and allow data to be manipulated. All non-destructive instruments should be calibrated frequently and regularly by the inspector, preferably using a procedure agreed upon by the parties concerned. Film thickness is so often a source of argument that all relevant details should be decided upon during the preliminary discussions, e.g. criteria of film thickness, instruments to be used and how they are to be calibrated. Time spent on this will be recouped many times over in delays avoided during the running of the contract.

Working Conditions

Good conditions of work, e.g. adequate ventilation, control of temperature, shelter from the elements, etc. which should be provided for the operators in any case, are, in the majority of coating operations, also vital to the success of long-life systems. Appropriate conditions are now specified for most contracts and it is for the inspector to see that they are not exceeded. He should be provided with means to measure steel temperature, wet-and-dry bulb hygrometer and any air-sampling instruments that may be necessary for work in special areas or confined spaces. In particular, he will be watching for moisture, dust or debris (falling or wind-borne) which may contaminate painting which is in process, or before it is sufficiently dry.

Sampling and Testing

There are two ways of checking materials for a protective coating contract. Firstly, by sampling at the point of manufacture and/or after delivery at the coating works, and secondly by taking samples of the materials in use.

Testing of Supplies

For many government contracts and for most major projects, or where the performance of the coating is vital, supplies of paint are often sampled at the manufacturer's works and checked in a laboratory to ensure that they conform to the standard specified. This may be a written standard for composition or performance or a proprietary paint which has been approved by long experience or special trials.

Laboratory tests may also be carried out to test such properties as viscosity, specific gravity, drying time, fineness of grind, adhesion to steel and percentages of the volatile constituent and non-resin solids. If these tests have been carried out on a sample of the paint as originally approved, then the results can comprise a suitable standard for any batch testing. Approved batch numbers or passing certificates may then be forwarded to the inspector for checking against deliveries.

Testing of Materials in Use

As already stated, it must be one of the inspector's duties to see that the materials delivered conform to the specification, or to any subsequent modification which may have been agreed. Similar tests to those outlined above may be carried out, either on site or in the laboratory.

The abrasive in use should not be ignored by the inspector. He should have a standard reference sample in order to be able to determine when the grade is wrong or the grit is dirty.

Whatever samples are taken from materials in use, whether tested or not, they should be preserved for a reasonable time, at least until the end of any maintenance period under the contract.

Conclusion

It can be seen from what has been said that the technology of surface preparation and coating application is complex. Attention to detail cannot be ignored and every effort must be made to train painting inspectors as well as possible. Certification schemes are, without doubt, a positive step in this direction and should be supported.

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20 ELECTROCHEMISTRY AND METALLURGY RELEVANT TO CORROSION

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20.1 Outline of Electrochemistry

The present Section, which provides an outline of selected relevant topics in electrochemistry, is intended primarily as an introduction to aqueous corrosion for those readers whose basic training has not involved a study of electrochemistry. The scope of electrochemistry is enormous and cannot be treated adequately here, but there are now a number of excellent books on the subject, and it is hoped that this outline will serve to stimulate further study. The topics selected are as follows: (a) the nature of the electrified interface between the metal and the solution, (b) adsorption, (c) transfer of charge across the interface under equilibrium and non-equilibrium conditions, (d) overpotential and the rate of an electrode reaction and (e) the hydrogen evolution reaction and hydrogen absorption by ferrous alloys. For reasons of space a number of important topics, such as the electrochemistry of electrolyte solutions, have been omitted.

In this outline some emphasis has been given to the nature of the electrified interface that exists between an electrode and a solution and on adsorption of intermediate species at the interface; aspects of electrochemistry that are frequently disregarded in accounts of the electrochemical mechanism of corrosion. The fact remains that adsorption of species from solution at the interface is normally a precursor to a corrosion reaction and will dictate the form it takes, its rate, and its location on a heterogeneous metal surface. Unfortunately, although knowledge on the adsorption on a mercury electrode is advanced the position is quite different in the case of industrial metals and alloys, and this has limited our understanding of a variety of phenomena in corrosion such as pitting, stress-corrosion cracking, etc. Nevertheless, an understanding of the nature of the electrified interface is essential for an appreciation of the detailed mechanisms of corrosion.

The Electrified Interface

An aqueous electrolyte solution consists of a variety of charged and uncharged species, e.g. cations, anions, water dipoles, organic molecules, trace impurities, etc. which under equilibrium conditions are randomly oriented so that within the solution there is no net preferentially directed field. However, under the influence of a potential difference, the charge will be transported through the solution by cations and anions that migrate to

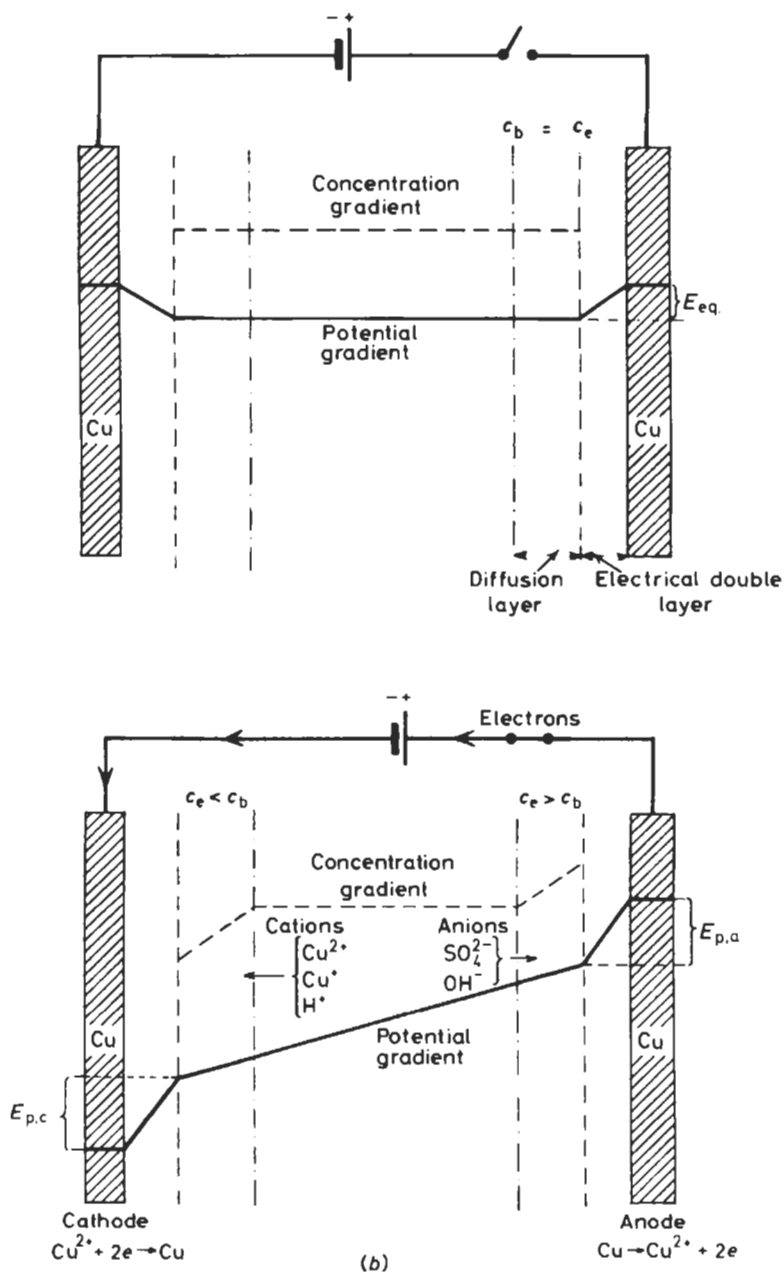
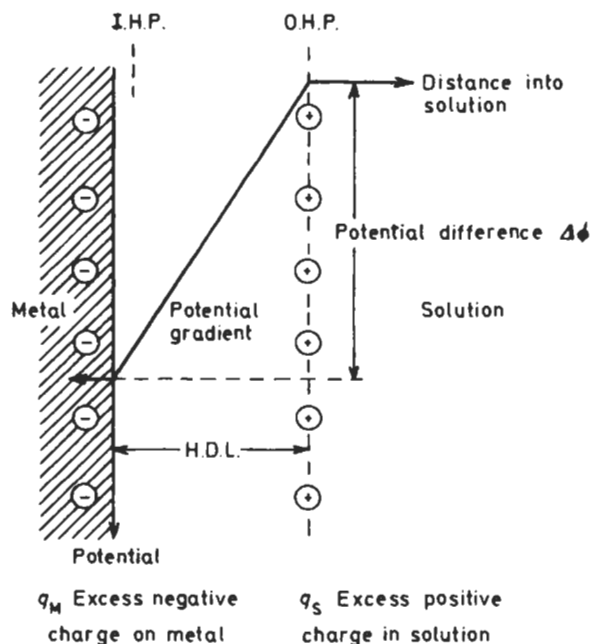


Fig. 20.1 Potential and concentration gradients in the electrolytic cell $\text{Cu}/\text{CuSO}_4/\text{Cu}$. (a) The electrodes are unpolarised; the potential difference is the equilibrium potential E_{eq} , and there is no concentration gradient in the diffusion layer. (b) The electrodes are polarised; E_p of the anode is now more positive than E_{eq} , whilst E_p of the cathode is more negative and concentration gradients exist across the diffusion layer; c_e , c_b , are the concentrations at the electrode and in the bulk solution



A simplified diagram of the Helmholtz double layer as a capacitor. It consists of two vertical parallel lines. The left line has several minus signs (-) on its left side. The right line has several plus signs (+) on its right side. A diagonal line connects the two vertical lines, representing the potential gradient. Below the diagram, the equation is given: $C = \frac{\text{charge}}{\text{p.d.}} = \frac{q}{\Delta\phi}$.

Fig. 20.2 Helmholtz double layer (H.D.L.) consisting of a 'plate' of excess negative charges on the surface of the metal and a counterbalancing 'plate' of excess positive charges (cations) in solution, the double layer as a whole being electrically neutral. The double layer can be regarded as equivalent to a capacitor in which the 'plates' are separated by a distance δ

the cathode and anode, respectively; this migration of charge through an electrolyte is responsible for *electrolytic conduction*. At each electrode there will be a transfer of electrical charge and a consequent electrode reaction that results in a change in the concentration of the reacting species at the surface of the electrode. Under these circumstances the transport of species to and from the electrodes is by diffusion and convection as well as migration; the term *transport* is used here to include diffusion, convection and migration.

Figure 20.1 shows the potential differences and concentration gradients in the cell $\text{Cu}/\text{CuSO}_4/\text{Cu}$.

Similarly, all points within a metal, which consists of an ordered rigid lattice of metal cations surrounded by a cloud of free electrons, are electrically neutral. Transport of charge through a metal under the influence of a potential difference is due to the flow of free electrons, i.e. to *electronic conduction*. The simultaneous transport of electrons through a metal, transport of ions through a solution and the transfer of electrons at the metal/solution interfaces constitute an electrochemical reaction, in which the electrode at which positive current flows from the solution to the electrode is the *cathode* (e.g. $M^{z+}(\text{aq.}) + ze \rightarrow M$) and the electrode at which positive flows from it to the solution (e.g. $M \rightarrow M^{z+}(\text{aq.}) + ze$) is the *anode*.

At any interface between two different phases there will be a redistribution of charge in each phase at the interface with a consequent loss of its electro-neutrality, although the interface as a whole remains electrically neutral. (Bockris¹ considers an *interface* to be sharp and definite to within an atomic layer, whereas an *interphase* is less sharply defined and may extend from at least two molecular diameters to tens of thousands of nanometres; the interphase may be regarded as 'the region between the two phases in which the properties have not yet reached those of the bulk of either phase'.) In the simplest case the interface between a metal and a solution could be visualised as a line of excess electrons at the surface of the metal and an equal number of positive charges in the solution that are in contact with the metal (Fig. 20.2). Thus although each phase has an excess charge the interface as a whole is electrically neutral.

The separation of charge at a metal/solution interface results in a strong electric field in the space between the charged layers and a potential difference across the extremities, and although the potential differences are comparatively small ($< 1.0 \text{ V}$), the small distance of separation of the charged layers results in a very high field strength; taking the distance of separation as 0.1 nm and the potential difference as 1 V , the field strength (potential difference/distance) will be approximately 10^7 V cm^{-1} (10^9 V m^{-1}). This high field strength is responsible for the facility with which electrons can cross the interface during electrode reactions, and a very small change in the excess charge at the interface can have a very significant effect on the potential difference and the velocity of the electrode process. Thus it can be calculated² that for a cathodic process involving one electron an excess charge of only approximately 0.1 C m^{-2} ($1 \text{ mol of electrons} \equiv 1 \text{ F} \approx 96\,500 \text{ C}$, so that $0.1 \text{ C} \approx 10^{-6} \text{ mol of electrons}$) will change the potential difference by as much as -0.6 V , and could increase the rate of the process by a factor of 10^5 .

Structure of the Electrical Double Layer (E.D.L.)

A simple model of the e.d.l. was first suggested by Helmholtz in which the charges at the interface were regarded as the two plates constituting a parallel plate capacitor, e.g. a 'plate' of metal with excess electrons (the inner Helmholtz plane I.H.P.) and a 'plate' of excess positively charged ions (the outer Helmholtz plane O.H.P.) in the solution adjacent to the metal; the

charges balance one another so that the e.d.l. is neutral as a whole (Fig. 20.2). Although this model, which is based entirely on electrostatic concepts, is applicable under certain circumstances it has certain limitations and is incapable of explaining a number of experimental observations. Thus although on the basis of the Helmholtz model the distance of separation of charges is taken as approximately 0.1 nm (the diameter of an ion) the inter-phase actually extends to at least 0.5 nm and can affect the adsorption of species at even greater distances.

If it is assumed that the interface between mercury (which is widely used as an electrode for studies of the e.d.l.) and an electrolyte solution forms the two plates of a capacitor, then at equilibrium the mercury 'plate' will have an excess charge q_{Hg} and the solution 'plate' a charge of equal magnitude but opposite sign q_s , and the capacitance C is given by

$$C = \frac{q_{\text{Hg}}}{\Delta\phi} \quad \dots (20.1)$$

where $\Delta\phi$ is the potential difference. On the basis of this model the potential difference between the 'plates' due to excess charge is

$$\Delta\phi = \frac{q\delta}{\epsilon_r \epsilon_0} \quad \dots (20.2)$$

where ϵ_r is the relative permittivity of the 'material' between plates, ϵ_0 is the permittivity of a vacuum ($8.85 \times 10^{-12} \text{ Fm}^{-1}$) and δ is the distance between the plates.

In this connection it is necessary to consider the contribution made to the potential difference by the dielectric itself, and in aqueous solution this will be largely due to adsorption of water molecules, although adsorption of other molecules in solution can also have an effect. Although the water molecule is electrically neutral as a whole, the fact that the two binding electrons are closer to the oxygen atom than to the hydrogen atoms results in an electric dipole with a positively charged (hydrogen) end and a negatively charged (oxygen) end, and consequently a potential difference exists across the molecule (Fig. 20.3a).

If the metal has a large negative excess charge the adsorbed water molecules will be oriented with their positive ends towards the metal and their negative ends towards the solution, and this layer of oriented dipoles will contribute an additional potential difference to the double layer (Fig. 20.3b). The converse situation will arise when the metal has a large positive charge, and again the dipoles will contribute to the potential difference (Fig. 20.3c). In the case of a metal with only a small excess charge dipoles of both orientations will adsorb, and the potential difference will be proportional to the excess number of one or the other (Fig. 20.3d).

Thus the potential difference at the interface between a metal and electrolyte solution is due to both the charges at the interface (electrostatic potential difference) and the surface dipole layers; the latter is referred to as the *surface* or *adsorption* potential difference. On the basis of the above considerations it might appear that adsorption at a metal surface with an excess charge is solely due to electrostatic interaction with charged species in the solution, i.e. if the metal surface has an excess negative charge the cations

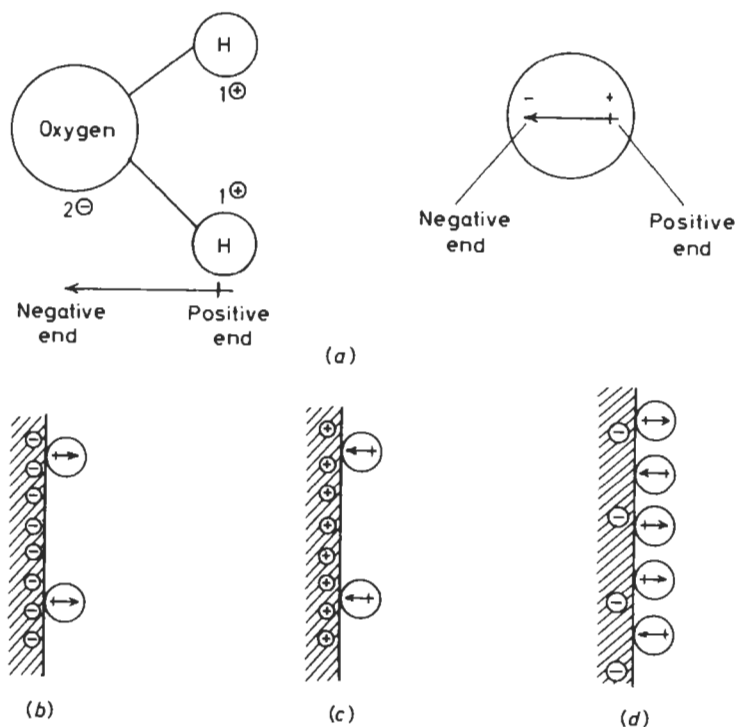


Fig. 20.3 Adsorption of water dipoles. (a) A water dipole showing the positive hydrogen end and negative oxygen end, (b) adsorption on metal with large negative excess charge, (c) adsorption on metal with large positive excess charge and (d) adsorption on metal with small negative excess charge

are attracted to the surface and adsorb, whereas the anions because of electrostatic repulsion are prevented from adsorbing. However, this simple model takes no account of *specific* or *contact* adsorption, and as will be discussed subsequently it is possible for negatively charged anions to adsorb strongly on the surface of a metal that has a negative excess charge.

Electrocapillary Curves and Excess Charge of an Interface

At the surface of a liquid the surface molecules will be subjected to a strong inward attraction due to molecules in the interior and to a much weaker force due to the molecules of the gaseous phase. This gives rise to a surface tension (or to an interfacial tension if two liquids are involved) which tends to cause the surface to shrink to give the minimum surface area; thus droplets of liquid and bubbles tend to take up a spherical shape, since a sphere has the minimum surface area for a given volume. Surface tension is also responsible for a liquid rising up a very fine capillary. On the other hand, when there is an excess charge at an interface the ions comprising the excess charge will repel one another and this will result in a tendency for the surface to expand; the forces due to the molecular attraction, interfacial tension and

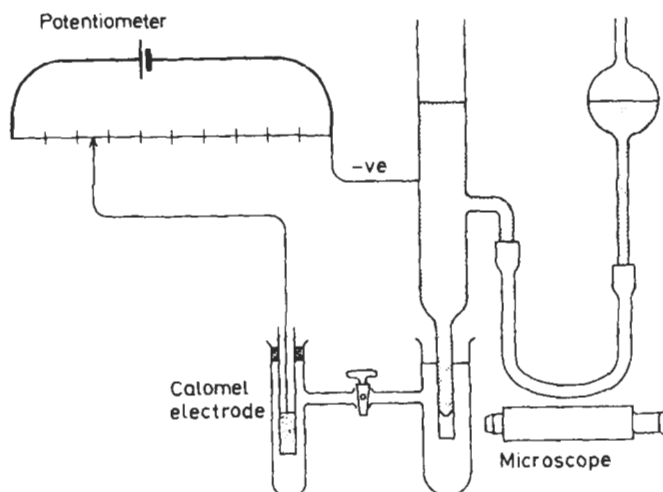


Fig. 20.4 Lippmann electrometer for studying the variation of the excess charge on mercury with variation in potential difference at the mercury solution interface

those due to the excess charge thus oppose one another, and this effect can be used to study the variation of excess charge with the potential of the interface. The excess charge at a mercury/electrolyte solution interface has been extensively studied by the Lippmann electrometer (Fig. 20.4), in which mercury in a fine capillary is in contact with the solution under study. The potential of the mercury, which tends to be positive in most aqueous solutions, can be varied by means of a potentiometer and its potential measured by a suitable reference electrode. A change in the potential of the mercury/solution interface will result in a displacement of the mercury in the capillary, which can be determined with respect to a reference mark on the capillary by means of a travelling microscope. The solutions selected for these studies and the potential must be such that no electrode reactions occur, and under these conditions the applied potential builds up a charge at the highly polarisable mercury/solution interface, the magnitude of which can be determined by the displacement of the mercury meniscus.

Electrocapillary curves are obtained by plotting the interfacial tension γ (displacement of mercury expressed in appropriate units) against potential difference at the mercury/solution interface with respect to a reference electrode. Figure 20.5 shows how the interfacial tension increases as the potential difference between the interface and the reference electrode is increased (in Fig. 20.5 the interface is made more negative), until it reaches a maximum when further increase in potential results in a corresponding decrease in the interfacial tension. The excess charge q_M , or *charge density*, at constant temperature T , pressure p and concentration of electrolyte c is given by the Lippmann equation

$$q_M = - \left(\frac{\partial \gamma}{\partial \Delta \phi} \right)_{T, p, c} = - \left(\frac{\partial \gamma}{\partial E} \right)_{T, p, c} \quad \dots (20.3)$$

in which γ is the interfacial tension and $\Delta\phi$ is the potential difference between the mercury and the solution. It should be noted that the absolute value of $\Delta\phi$ cannot be determined, but since it is only differences in potential that are significant the change in the interfacial potential difference $\Delta\phi$ will correspond to the potential difference E determined by means of a suitable reference electrode (see Section 20.2).

If the electric double layer is regarded as a simple parallel-plate condenser the electrocapillary curve should take the form of a perfect parabola consisting of an ascending positive branch (excess positive charge on mercury and counterbalancing layer of negative charges in the solution) and a descending negative branch (excess negative charge on mercury and counterbalancing layer of positive charges in the solution). Solutions of different alkali nitrates at the same concentration give electrocapillary curves that coincide and that approximate to a perfect parabola, in spite of the fact that the cations that adsorb on the negative branch of the curve (Na^+ , K^+ , etc.) are different. However, in the case of the potassium halides (Fig. 20.5), although the negative branches of the curve (adsorption of K^+) are similar, marked divergences are obtained on the positive branch of the curve

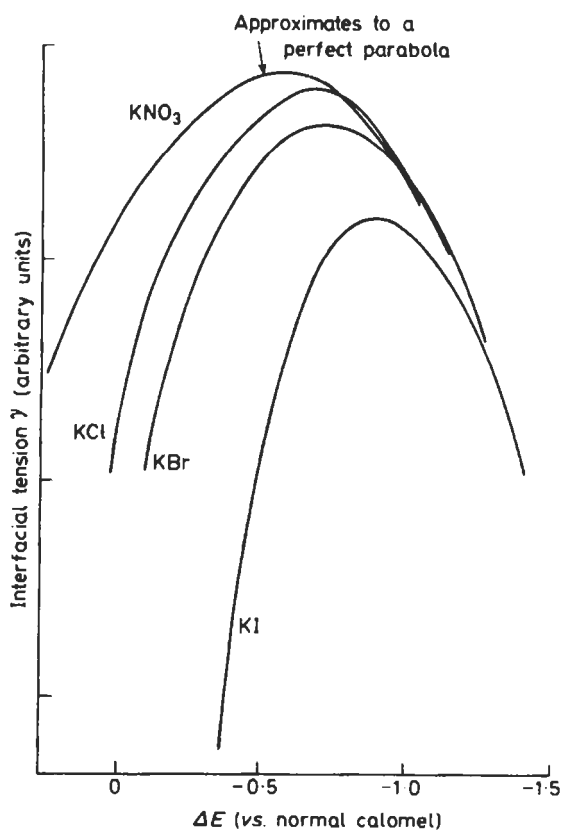


Fig. 20.5 Electrocapillary curves for KNO_3 , and different potassium halides showing how the former approximates to a parabola

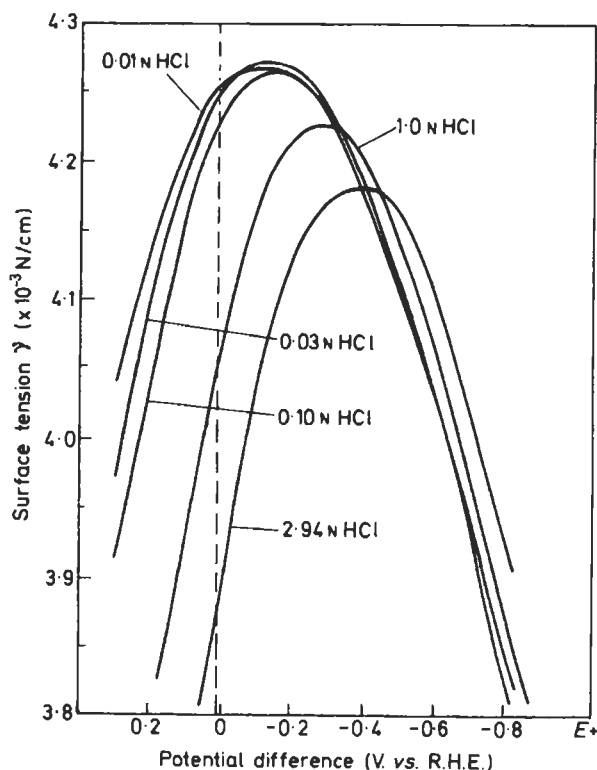


Fig. 20.6 Electrocapillary curves for HCl at various concentrations determined using a reversible hydrogen electrode (R.H.E.) immersed in the same concentration of HCl as that used for the determination (after Bockris and Reddy¹)

(adsorption of halide), and it can be seen that the divergences from ideality are in the order $I^- > Br^- > Cl^-$. In general, the departure of the curve from ideality occurs on the positive ascending branch at which anions are adsorbed at the mercury/solution interface.

Similar considerations apply to the curves obtained for a single electrolyte at different concentrations¹ (Fig. 20.5), and in the case of HCl whereas the ascending branches of the curves (adsorption of Cl^-) show divergences that increase with increase in concentration, the descending branches of the curves (adsorption of H^+) almost coincide. Thus again it is the anion rather than the cation (only large organic cations such as the tetra-alkylammonium ion have a significant effect) that affects the shape of the electrocapillary curve.

Potential of Zero Charge¹⁻³

The gradient of the electrocapillary curve (equation 20.3) at a given potential gives the charge density at that potential, and it is evident from the slopes that it will be positive on the ascending branch and negative on the descending branch. At the electrocapillary maximum, however, the gradient is zero.

$$q_M - \left(\frac{\partial \gamma}{\partial E} \right) = 0 \quad \dots (20.4)$$

and there will be no excess charge at the interface. The potential corresponding to the electrocapillary maximum is referred to as the *potential of zero charge* (p.z.c.) and is given the symbol $E_{\text{p.z.c.}}$, and reference to Figs. 20.5 and 20.6 shows that it varies with the nature of the anion and the concentration of the electrolyte.

In the case of Hg, Ga and liquid amalgams, the p.z.c. at ambient temperatures can be determined from the electrocapillary curve, and this method has also been used for molten metals in molten electrolytes at elevated temperatures. Other methods³ that have been used to determine the p.z.c. are based on the variation of some property of the interface with variation in potential, e.g. (a) a change in contact angle between a gas bubble and a metal surface immersed in an electrolyte solution, (b) a change in the capacitance of a metal, (c) variation in adsorption of a species from a solution, (d) a change in frictional properties, etc. Values for the p.z.c. for different metals obtained from various sources^{1,4,5} are given in Table 20.1. A recent method² is based on the principle that a change in the surface charge results in a very small change in the surface energy of the metal, which in turn causes distortion of the bulk metal, providing the latter is of very thin cross-section. This method is similar in certain respects to that used for determining stress in electrodeposits by measuring the distortion produced in a thin metal substrate. The metal to be studied is sputtered as a very thin layer (<10.0 nm) onto a thin substrate (<0.01 cm thick) immersed in the solution, and the very small distortions obtained when the potential is varied are determined by means of a laser beam.

Table 20.1 Potential of zero charge $E_{\text{p.z.c.}}$ and $E_{M^{z+}/M}^{\ominus}$ of metals

<i>Metal</i>	$E_{\text{p.z.c.}}$ (V, vs. S.H.E.)	<i>Equilibrium</i>	$E_{M^{z+}/M}^{\ominus}$ (V)
Cd (0.01 mol dm ⁻³ KCl)	-0.92	Cd ²⁺ /Cd	-0.42
Tl	-0.82	Tl ⁺ /Tl	-0.34
Ag (0.04 mol dm ⁻³ Na ₂ SO ₄)	-0.70	Ag ⁺ /Ag	+0.79
Ga	-0.60	Ga ³⁺ /Ga	-0.52
Al (0.01 mol dm ⁻³ KCl)	-0.52	Al ³⁺ /Al	-1.7
Fe (0.002 mol dm ⁻³ H ₂ SO ₄)	-0.37	Fe ²⁺ /Fe	-0.44
Bi (0.01 mol dm ⁻³ KCl)	-0.36		
Co (0.04 mol dm ⁻³ Na ₂ SO ₄)	-0.32	Co ²⁺ /Co	-0.27
Sb (0.01 mol ⁻³ HCl)	-0.19	Sb ³⁺ /Sb	
Hg	-0.19	Hg ²⁺ /Hg	+0.80
Ni	-0.06	Ni ²⁺ /Ni	-0.25
Cu (0.04 mol dm ⁻³ Na ₂ SO ₄)	+0.03	Cu ²⁺ /Cu	+0.34
Au (0.04 mol dm ⁻³ Na ₂ SO ₄)	-0.23	Au ³⁺ /Au	+1.3
Pt (0.003 mol dm ⁻³ HClO ₄)	+0.41	Pt ³⁺ /Pt	+1.1

Although the p.z.c. is difficult to determine experimentally, and although the values obtained vary with the method used, it is of fundamental significance in electrochemistry, since it provides information on adsorption of ions and molecules, i.e. if the potential is negative with respect to the p.z.c. cations will tend to be adsorbed and anions repelled, and vice versa. The p.z.c. appears to be a natural reference point for a *rational scale* of potentials defined by

$$\bar{E} = E - E_{\text{p.z.c.}} \quad \dots (20.5)$$

where \bar{E} is the potential on the rational scale, E is the measured potential and $E_{\text{p.z.c.}}$ is the potential of zero charge (both E and $E_{\text{p.z.c.}}$ are with respect to the same reference electrode). The phi-scale of potentials, which has been developed largely by Antropov^{4,6}, takes a form that is similar to equation 20.5. It can be seen from Table 20.1 that $E_{M^{z+}/M}^{\circ}$ and $E_{\text{p.z.c.}}$ do not show any simple correspondence, and this is due to the fact that the former depends on the removal of an ion from the metal and its solvation (see p. 20.85) whilst the latter is a function solely of the removal of an electron from the metal, i.e. of the electronic work function.

Adsorption

The adsorption of ions and molecules at an electrified interface is of fundamental importance in all aspects of aqueous corrosion, and it is therefore relevant to consider it briefly in the context of this discussion on the nature of the electrified interface^{1,2,7}. Gases may be adsorbed on solid surfaces in various ways, and when the adsorbed layer is held by the residual forces around the gas molecule, which are responsible for the liquefaction of gases and the cohesion in liquids, it is referred to as *physical or van der Waals* adsorption. Physical adsorption is reversible and the adsorbed gas can be removed by evacuation or by heating to moderate temperatures; the enthalpy of physical adsorption is small ($< 1 \text{ kJ mol}^{-1}$). In *chemisorption* the adsorbed layer is chemically combined by covalent (or ionic) forces to the metal, and removal of the layers requires evacuation at high temperatures; the enthalpy of chemisorption is at least approximately 2 kJ mol^{-1} and the bond between the metal and the surface is almost as strong as in stoichiometric compounds. An example of chemisorption is the adsorption of hydrogen gas onto the surface of tungsten, during which the hydrogen molecules in contact with the surface dissociate and form a chemical bond, with each atom of hydrogen combining with an atom of tungsten to form a monolayer. This dissociation of the hydrogen molecules and the formation of a bond takes place over a distance of 0.1 nm . Physical adsorption and chemisorption are not mutually exclusive and both can occur in certain systems. Thus when oxygen is adsorbed on charcoal, part is physically adsorbed and is readily removed by evacuation whilst the remainder is chemisorbed, and although it can be removed by evacuation at elevated temperatures the gases evolved consist of the oxides of carbon showing that the bond between the oxygen and carbon is greater than that between the carbon atoms in the solid.

In adsorption at an electrified interface the electric field is long range and can influence ions some distance into the solution away from the metal surface, and this *electrostatic* adsorption may extend to 100 nm . However, within $0.1\text{--}0.2 \text{ nm}$ of the surface there will also be some degree of chemisorption of ions that are in contact with the metal surface, which is referred to as specific or contact adsorption. Thus in considering adsorption at a charged interface, account must be taken of both the long-range electrostatic forces and the short-range chemical forces.

The adsorption of ions due to an electrified interface can be evaluated by considering a series of laminae of the solution at various distances from the metal surface and assessing the number of ions present as compared with those that would have been present if the electrified interface had been

absent. The sum of these excess ions, the 'Gibbs surface excess' Γ_i , is given by

$$\Gamma_i = \int_0^\infty \{c_i(x) - c_i^0\} dx = \frac{1}{S} \int_0^\infty \{c_i(x) - c_i^0\} dv$$

$$\therefore \Gamma_i = \frac{1}{S} \int_0^{n_i - n_i^0} d(\Delta n_i) = \frac{n_i}{S} - \frac{n_i^0}{S} \quad \dots (20.6)$$

where $c_i(x)$ is the actual concentration of the species i at a distance x from the metal surface, c_i^0 the concentration in the bulk solution (where the electrified interface has no influence), n_i the actual number of moles of i in the interphase region, n_i^0 the number of moles of i that would be present if the electrified interface were absent, S the area of the interphase and v the volume of the solution. It is evident that Γ_i will be either positive or negative depending on whether n_i is larger or smaller than n_i^0 , respectively.

The Gibbs adsorption equation for the adsorption of an ion i from solution can be written in the form of the thermodynamic equation

$$(\Gamma_i)_E = -\frac{1}{2RT} \left(\frac{\partial \gamma}{\partial \ln a_i} \right)_{T, x, o} \quad \dots (20.7)$$

where a_i is the activity of the ion and the subscript E signifies that the surface excess Γ_i is measured at constant potential. In measuring the potential of a mercury solution interface (a polarisable electrode) it is necessary to measure the e.m.f. of a cell consisting of that interface and a non-polarisable reference electrode. It can be shown on the basis of thermodynamic arguments that equation 20.7 is applicable only if the reference electrode is reversible to an ion j of opposite sign to i . Thus if information is required on the adsorption of anions (e.g. Cl^- ions) then the reference electrode must be reversible to cations (e.g. a reversible hydrogen electrode); if information is required on the adsorption of cations the reference electrode must be reversible to anions (e.g. a calomel electrode).

It follows that the surface excess Γ_- of an anion i (e.g. the Cl^- ion) can be evaluated from the electrocapillary curves of a given electrolyte (e.g. HCl) by plotting surface tension against the logarithm of the activity of the electrolyte (evaluated at various constant potentials) and determining the slope of the curve $\partial \gamma / \partial \log a_i$ and introducing it into equation 20.7.

The total excess charge q_s in solution is due to both anions and cations, and is given by

$$q_s = z_+ F \Gamma_+ + z_- F \Gamma_- \quad \dots (20.8)$$

and since q_M is given by equation 20.3 and is equal to $-q_s$ it is possible to evaluate the surface of the cation Γ_+ from q_M and Γ_- since

$$z_+ F \Gamma_+ = q_s - z_- F \Gamma_- \quad \dots (20.9)$$

The above provides a means of showing how the total excess charge on the solution side of the interface q_s , the excess charge due to cations Γ_+ and the excess charge due to anions Γ_- , vary with potential in a solution of fixed concentration of electrolyte. On the basis of this approach to the electrocapillary curves it has been shown that the Gibbs surface excess for cations is due solely to electrostatic forces (long-range coulombic), and this is reflected in the fact that the electrocapillary curves for different cations and

the same anion at the same concentration (e.g. alkali nitrates) coincide, i.e. specific or contact adsorption is absent. On the other hand, adsorption of anions can only be explained by taking into account both electrostatic and contact adsorption.

Inconsistencies of the Parallel Plate Model

The simple Helmholtz model, in which the charge on the model is regarded as the plate of a capacitor that attracts a counter layer of ions of opposite charge and results in two parallel plates of the same charge density, is inconsistent with the shapes of the electrocapillary curves obtained in practice. It can be shown^{1,2} that if the Helmholtz model applied, the electrocapillary curve would conform to the relationship

$$\gamma = \gamma_{\max.} - \frac{\epsilon}{4\pi\delta} \times \frac{1}{2} E^2 \quad \dots (20.10)$$

where $\gamma_{\max.}$ corresponds with the electrocapillary maximum. This is the equation for a parabola, symmetrical about $\gamma_{\max.}$, and it is evident that this is seldom achieved in electrolyte solutions, particularly when the electrolyte is a halide (Figs 20.5 and 20.6).

A further inconsistency in the Helmholtz model is revealed by the differential capacitance C which is given by

$$C = \left(\frac{\partial q_M}{\partial E} \right)_{\text{const. comp.}} = \frac{\epsilon_r \epsilon_0}{\delta} \quad \dots (20.11)$$

and which can be evaluated, at any given value of E , from the slope of the electrocapillary curve. Since ϵ_r , ϵ_0 and δ should be constant, the curve of electrode charge *vs.* potential should be linear, and C (the slope of the curve) should remain constant at all values of E . Figure 20.7 shows results

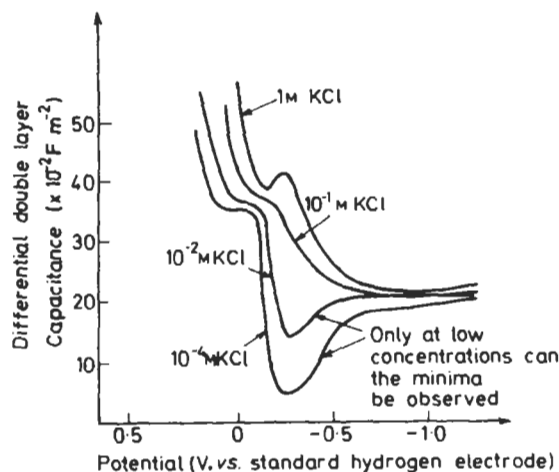


Fig. 20.7 Differential capacitance/mercury electrode potential relationships for potassium chloride at different concentrations showing (a) how minima are obtained only at low concentrations and (b) the constant capacitance at negative potentials (after Bockris and Drazic²)

obtained for Hg in solutions of KCl at different concentrations, and it can be seen that C varies with potential and concentration except at very negative potentials where it is almost constant. This constant capacitance has been found to be independent of the nature of the ion, although if δ is taken as the distance between the electrode and the centres of the ions on the solution side of the interface it should vary with the ionic radius of the ion (equation 20.11). It should be noted that at the intermediate potentials the curves for dilute solutions approximate to inverted parabolas.

Gouy–Chapman and Stern Models of the Double Layer

Gouy and Chapman (1910) pointed out that the Helmholtz model could not provide a true picture of the double layer, since the disordering forces due to the thermal energy of the ions would oppose their ordering by electrostatic forces. This would result in an equilibrium in which the excess of the counter ion would be a maximum close to the surface of the electrode and would diminish gradually with increasing distance from the surface (Fig. 20.8). In many respects this diffuse charge model is similar to that used by Debye and Hückel in their theory of interionic attraction of ions in solution, in which the ion is regarded as a point charge having a spherically symmetrical field which diminishes with distance from the ion into the solution^{1,8}. Thus the

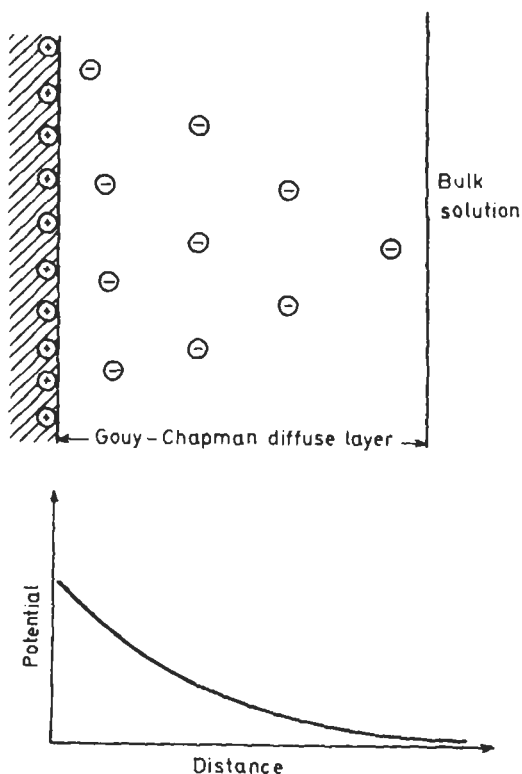


Fig. 20.8 Gouy–Chapman diffuse layer model of the double layer

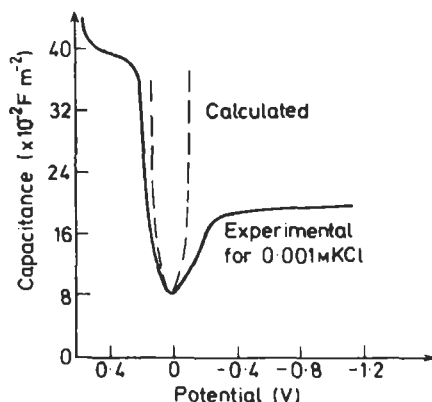


Fig. 20.9 Experimental capacitance–potential curve for 0.001 M KCl and calculated curve using the Gouy–Chapman model. The experimental curve and the theoretical curve agree at potentials (vs R.H.E.) near the p.z.c. Note the constant capacitance of $\approx 17 \times 10^{-2} \text{ F m}^{-2}$ at negative potentials (after Bockris and Drazic²)

potential in an electrode–ion interaction should be a maximum at the metal surface, and should decay exponentially with distance into the solution and attain a constant value (zero) in the bulk solution.

The Gouy–Chapman theory predicts that the differential capacitance of the interface should be a hyperbolic cosine function of the potential difference, and this should result in a curve that takes the form of an inverted parabola. Figure 20.9 shows the differential capacity against potential curves calculated on the basis of the Gouy–Chapman model and the experimental values obtained for 0.001 M KCl, and it can be seen that there is fair agreement only at potentials close to the p.z.c. Thus although the model is applicable to ions whose thermal energy is of the same order as their energy of interaction with the electrode field, it is not applicable to those ions that are adsorbed in the Helmholtz double layer.

The Stern model (1924) may be regarded as a synthesis of the Helmholtz model of a layer of ions in contact with the electrode (Fig. 20.2) and the Gouy–Chapman diffuse model (Fig. 20.10), and it follows that the net charge density q_s on the solution side of the interphase is now given by

$$q_s = q_H + q_G = -q_M \quad \dots (20.12)$$

where q_H is the charge stuck to the electrode (Helmholtz model) and q_G is the charge diffusely spread out in solution (Gouy–Chapman model). Thus although the interphase region as a whole remains electrically neutral the model leads to the concept of two distinct regions of charge separation:

1. The interface region from the electrode to the Helmholtz plane (the locus of the centres of the ions in contact with the electrode) across which the potential varies linearly.
2. The region from the Helmholtz plane into the solution, across which the potential varies exponentially attaining a value of zero at some distance; in this region the ions are subjected to both ordering electrical forces and disordering thermal forces.

The Stern model predicts that the total differential capacitance C will consist of two terms representing two capacitors in series

$$\frac{1}{C} = \frac{1}{C_H} + \frac{1}{C_G} \quad \dots (20.13)$$

where C_H is the Helmholtz capacity of the region between the metal and the O.H.P., and C_G is the capacity of the diffuse charge. It can be shown that when the concentration of the electrolyte is large most of the charge is confined in or near the Helmholtz double layer with little charge scattered in the diffuse layer, and under these circumstances

$$\frac{1}{C} \approx \frac{1}{C_H}, \text{ or } C \approx C_H \quad \dots (20.14)$$

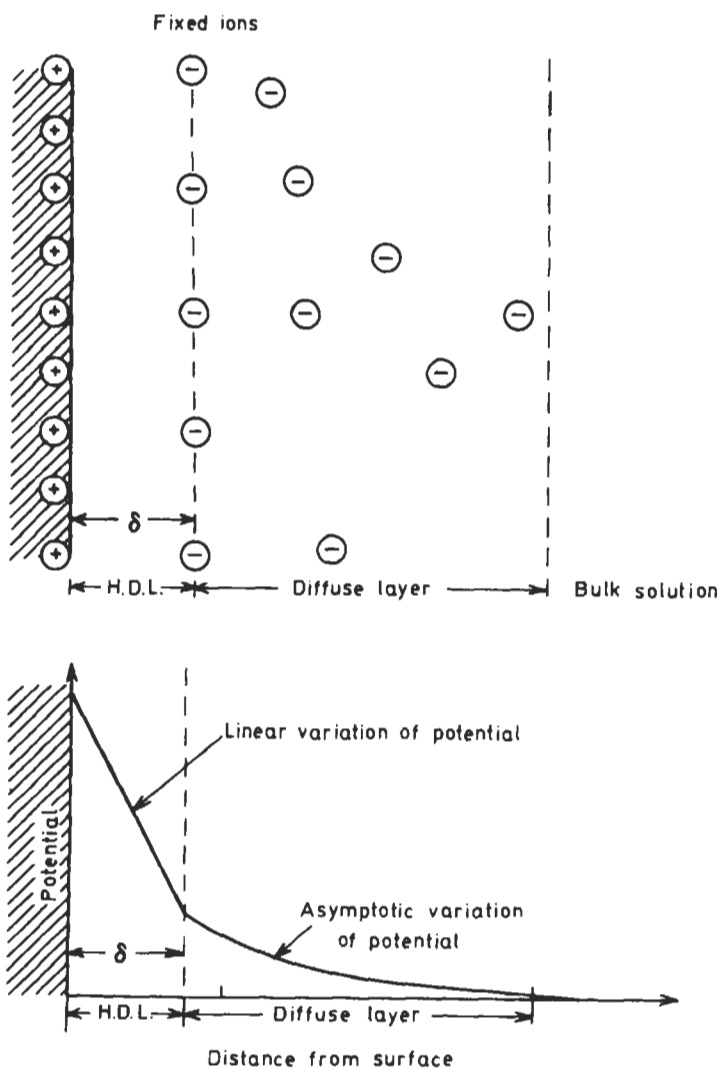


Fig. 20.10 Stern model of the double layer

which means that in concentrated solutions the diffuse layer can be neglected and the double layer approximates to the Helmholtz model. Conversely, in dilute solutions

$$\frac{1}{C} \approx \frac{1}{C_G}, \text{ or } C \approx C_G \quad \dots (20.15)$$

and the double layer approximates to the Gouy-Chapman model.

Structure of the Double Layer

Previous considerations have indicated that the simple Helmholtz double layer could be regarded as analogous to a capacitor in which the layer of excess charge on the metal (the I.H.P.) forms one plate and the counter-balancing layer of ions in solution (the O.H.P.) forms the other (Fig. 20.2). If the solution is concentrated the Gouy-Chapman diffuse layer may be disregarded, although it will exist and will provide the small amount of excess charge needed to maintain electroneutrality of the interphase as a whole.

Two alternative structures for the simple Helmholtz double layer (Fig. 20.11) have been provided¹:

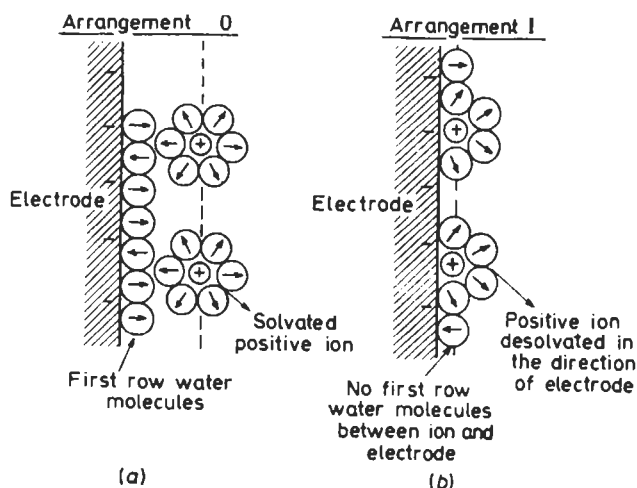


Fig. 20.11 Two types of arrangement of ions at a metal/solution interface. (a) Arrangement 0; solvated ions in the O.H.P. and surface of electrode covered with water dipoles. (b) Arrangement I; desolvated ions in the I.H.P. (after Bockris and Reddy¹)

1. Arrangement 0, in which water dipoles completely cover the surface of the metal with the locus of the centres of the hydrated ions forming the O.H.P.
2. Arrangement I, in which ions stripped of their solvent sheath are in direct contact with the metal.

Arrangement O is based on the hypothesis that the surface of the electrode is covered with water molecules, and it can be calculated from the number of water molecules per cm^2 on a plane in water and from the number of metal atoms per cm^2 (adsorption sites), that at least 70% of the surface is covered with water molecules, i.e. coverage $\theta > 0.7$. Furthermore, image forces, dispersion forces and covalent bonding can increase coverage still further so that the majority of the sites will be occupied by water molecules, and if the electrode is electrically charged the field perpendicular to the electrode will result in the orientation of the adsorbed water dipoles (Fig. 20.3). Ions of opposite sign to that of the electrode, surrounded by their primary hydration sheath, will migrate to the electrode under the influence of the field until they collide with the oriented water dipoles of the hydrated electrode, but since the overlapping of the electron shells of the water molecules results in repulsion, they will not come into contact with it.

It is possible on the basis of this model (arrangement O) to explain the constant capacitance region on the negative side of the C vs. E curve (Fig. 20.7), and why the capacitance in this region is independent of the nature of the cations in the solution. The model of the double layer is shown in Fig. 20.12 in which it can be seen that the surface of the electrode and the

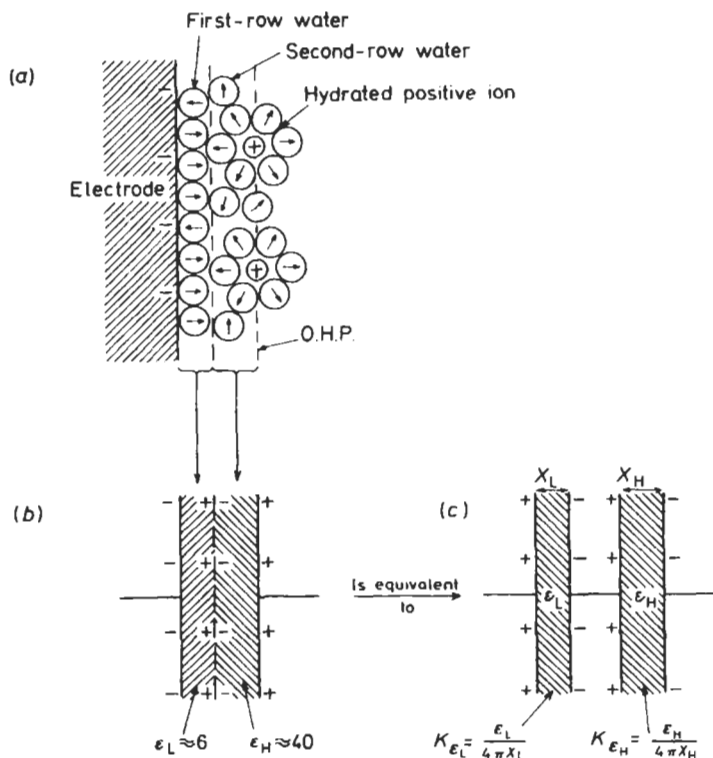


Fig. 20.12 Double layer consisting of (a) a layer of water dipoles and a layer of ions that may be regarded as (b and c) two capacitors in series (after Bockris and Reddy¹). Note that K_{ϵ_L} and K_{ϵ_H} are the capacitances of the regions of high and low permittivities, respectively

adsorbed water dipoles form one capacitor, whilst the second row of water molecules and the row of hydrated cations form the other, so that in effect there are two capacitors in series. If the total differential capacity of the double layer is C , then

$$\frac{1}{C} = \frac{1}{C_{\text{H}_2\text{O}}} + \frac{1}{C_{\text{H}}} = \frac{d_{\text{H}_2\text{O}}}{\epsilon_0 \epsilon_{\text{H}_2\text{O}}} + \frac{\epsilon_0 \epsilon_{\text{H}}}{(\delta - d_{\text{H}_2\text{O}})} \quad \dots (20.16)$$

where $\epsilon_{\text{H}_2\text{O}}$ is the relative permittivity of the layer of adsorbed water dipoles, ϵ_{H} that of the medium between the I.H.P. (locus of the centre of adsorbed water molecules) and the O.H.P. (locus of the centres of the hydrated ions), $d_{\text{H}_2\text{O}}$ the thickness of the water layer and $(\delta - d_{\text{H}_2\text{O}})$ the thickness of the remainder of the Helmholtz double layer. Water molecules adsorbed at an electrode will be completely oriented by the field, and will not be able to make the same contribution to the permittivity as is possible in bulk water in which they are free to orientate themselves. Under these circumstances $\epsilon_{\text{H}_2\text{O}}$ will be as small as approximately 5–6 (compared with 80 for bulk water), and since ϵ_{H} will be greater than 40 (approximating to the value of bulk water as the distance from the electrode increases) the 2nd term on the right-hand side of equation 20.16 will be small compared with the first and can be neglected. Taking $d_{\text{H}_2\text{O}} = 2.8 \times 10^{-2} \text{ m}$ and $\epsilon_0 = 8.85 \times 10^{-12} \text{ F m}^{-1}$, it can be calculated that $C \approx 17 \times 10^{-2} \text{ F m}^{-2}$ which is in good agreement with the capacity obtained experimentally (Fig. 20.9). This constancy of the differential capacity provides considerable support for the model shown in arrangement O, in which the capacitance is independent of the radius of the ions constituting the O.H.P.

In arrangement I (Fig. 20.11) it has been assumed that certain ions are able to divest themselves of their primary water sheath, push water dipoles away from the electrode and thus become adsorbed on the surface of the electrode. Thermodynamic calculations of the free energy of contact adsorption ΔG_{C} (the calculation involves a two-step process in which a certain number of water molecules become desorbed from the surface in the first step, whilst in the second step the ion divests itself of part of its water sheath and jumps into the hole) show that it is negative for certain ions (Cs^+ , Cl^- , Br^- and I^-) which should therefore be able to displace water and to adsorb on the metal surface, and positive for others (Na^+ , K^+ and F^-). There is a relationship between the free energy of contact adsorption and the ionic radius, and the larger the ionic radius the greater is the magnitude of $-\Delta G_{\text{C}}$; it follows that the larger the ionic radius (Table 20.2) the greater the tendency of the ion to adsorb at the surface of the electrode. The converse applies to ions of smaller ionic radius, which are so tightly bound to their solvent sheath that ΔG_{C} is positive and contact adsorption is not possible. Figure 20.13 shows the two possibilities, and it can be seen that in the absence of

Table 20.2 Ionic radii (nm)*

Li^+	0.068	Be^{2+}	0.035	F^-	0.133
Na^+	0.097	Mg^{2+}	0.066	Cl^-	0.181
K^+	0.133	Ca^{2+}	0.099	Br^-	0.196
Rb^+	0.147	Sr^{2+}	0.134	I^-	0.22
Cs^+	0.167	Ba^{2+}	0.134		

* Data from Parsons, R., *Handbook of Electrochemical Constants*, Butterworths, London (1959).

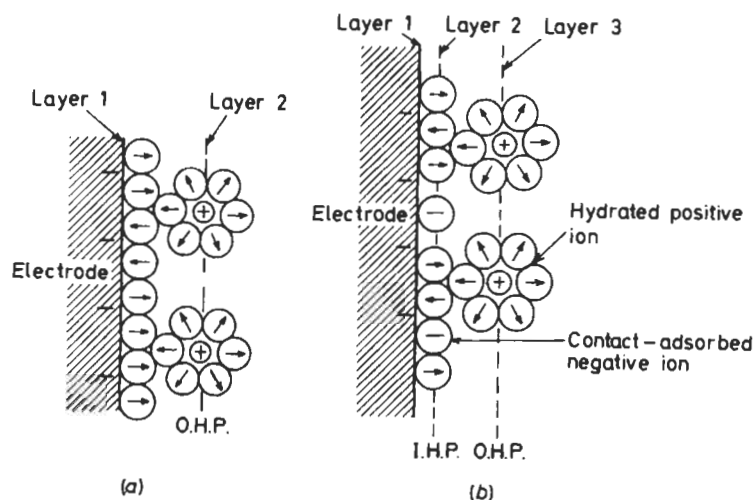


Fig 20.13 (a) Electrical double layer and (b) electrical triple layer (after Bockris and Reddy¹). Note that Layer 2 in (b) is produced by adsorption of negative ions on the negatively charged electrode

contact adsorption the double layer is similar to the Helmholtz model in which the layer of excess charge on the metal forms the I.H.P., whilst the counterbalancing layer of hydrated ions forms the O.H.P. The second possibility arises when contact adsorption occurs, the locus of the centres of the contact-adsorbed ions forming the I.H.P., and the locus of the centres of the hydrated ions the O.H.P. This model, which applies only when the solution is concentrated and contains ions of large ionic radius, is regarded by Bockris and Reddy¹ as giving rise to a *triple layer* (Fig. 20.13b).

It is important to note that the concept of contact adsorption resolves the problem of the adsorption of a negative ion on a negatively charged metal surface, which cannot be explained on the basis of simple coulombic forces; this difficulty was overcome formerly by referring to the phenomenon as *specific adsorption*, but it can now be interpreted in terms of contact adsorption involving short-range non-coulombic forces, i.e. image forces, dispersion forces and covalent bonding. It follows from the above that adsorption of Cl^- ions, a precursor to pitting, is possible even at potentials more negative than the p.z.c.

The majority of work on the electrified interface has been carried out using a mercury electrode, which has the advantage that it has a well-defined and reproducible surface and a highly polarisable interface when immersed in a solution. In the case of solid metals the concepts outlined are equally applicable, but modifications are necessary to allow for the following:

1. The non-electrostatic interaction between a solid metal and the constituents in solution (water, ions, etc.) will not be the same as that for mercury.
2. The degree of electrode polarisability differs, and most solid metals will be less polarisable than mercury. (See Section 20.3.)
3. The surface of mercury is homogeneous and all sites (Hg atoms) are equivalent, whereas a solid metal will have a heterogeneous surface with sites that differ in adsorption energies.

Adsorption Isotherms^{7,9}

An adsorption isotherm gives the relationship between the coverage of an interface with an adsorbed species (the amount adsorbed) and the pressure of gas or concentration of the species in solution; in electrochemical reactions the coverage will depend also on the potential difference at the interface.

Langmuir (1916), who put forward the first quantitative theory of the adsorption of a gas, assumed that a gas molecule condensing from the gas phase would adhere to the surface for a short time before evaporating and that the condensed layer was only one atom or molecule thick. If θ is the fraction of the surface area covered by adsorbed molecules at any time, the rate of desorption is proportional to θ and equal to $k_d\theta$ where k_d is a constant at constant temperature. Similarly the rate of adsorption will be proportional to the area of bare surface and to the rate at which the molecules strike the surface (proportional to the gas pressure p). At equilibrium the rate of desorption equals the rate of adsorption

$$k_d\theta = k_a(1 - \theta)p \quad \dots(20.17)$$

and the Langmuir isotherm can be expressed as

$$\frac{\theta}{1 - \theta} = \frac{k_a}{k_d}p = ap \quad \dots(20.18)$$

where a is a constant, the Langmuir constant or adsorption coefficient. Rearranging equation 20.18

$$\theta = \frac{ap}{1 + ap} \quad \dots(20.19)$$

Similarly, for adsorption of a species from solution

$$\theta = \frac{a'c_i}{1 + a'c_i} \quad \dots(20.20)$$

where c_i is the concentration of the species i in solution.

Two limiting cases of the Langmuir isotherm are of interest. When θ is very small, as when the pressure (or concentration) is low, or the constant a is small, then equation 20.18 reduces to

$$\theta = ap \quad \dots(20.21)$$

and θ is linearly related to p , a relationship that is observed frequently in the low-pressure region of the isotherm. When $\theta \rightarrow 1$, as at high pressures or with strong adsorption at low pressures, then the isotherm becomes

$$1 - \theta = \frac{1}{ap} \quad \dots(20.22)$$

and the fraction of the bare surface ($1 - \theta$) is inversely proportional to p , and θ tends to a limiting value in this region.

The Langmuir isotherm is based on the following assumptions:

- (a) The solid surface contains a fixed number of adsorption sites, and each site holds one adsorbed species.
- (b) The heat of adsorption is the same for all sites and is independent of θ .

- (c) The adsorbed species do not interact with one another so that a species may adsorb at an unoccupied site or desorb from an occupied site, irrespective of whether or not neighbouring sites are occupied.

The Langmuir isotherm has been found to be obeyed by a number of systems at low ($\theta < \text{approx. } 0.2$) or high ($\theta > \text{approx. } 0.8$) coverages, but fails in the intermediate region where the assumptions given above are no longer valid. Determinations of the heat of adsorption on clean metal surfaces shows that it frequently decreases markedly with increasing surface coverage, an observation that is indicative of surface non-uniformity. This non-uniformity is due to the intrinsic heterogeneity of the surface (edges of crystal growth planes, screw dislocations, kink sites, etc.) and to the repulsive forces between adsorbed atoms or molecules; the latter become very significant when the surface-to-adsorbate bond is partially ionic, since the repulsive forces are then large and result in a marked lowering of the heat of adsorption at the higher coverages.

Temkin suggested that the deviations from the Langmuir isotherm at high coverages could be accounted for by regarding the surface of the metal as being composed of small patches of equal size, at each of which the Langmuir isotherm holds independently with a characteristic local standard free energy of adsorption that depends on the patch distribution. The standard free energy of adsorption for each patch was assumed to decrease by equal small decrements over successively covered patches with increase in coverage, and the variation can be expressed by

$$\Delta G_\theta^\circ = \Delta G_0^\circ - fRT\theta \quad \dots (20.23)$$

where ΔG_0° and ΔG_θ° are the standard free energies of adsorption corresponding with $\theta = 0$ (the standard state) and finite θ , respectively. With these and other assumptions Temkin derived the isotherm

$$\theta = \frac{1}{f} \ln \left[\frac{1 + a_0 p}{1 + a_0 p \exp(-f)} \right] \quad \dots (20.24)$$

where a_0 is the value of the Langmuir constant (equation 20.18) for the first micro-adsorption patch covered ($\theta = 0$) and f is defined by equation 20.23, or by

$$f = \frac{1}{RT} \frac{d(\Delta G_\theta^\circ)}{d\theta} \quad \dots (20.25)$$

The factor f is thus a free-energy parameter, although it is usually the enthalpy of adsorption which is regarded as decreasing linearly with coverage in the intermediate region. Temkin pointed out that if f was sufficiently large, an intermediate range of values of p would exist where $a_0 p \gg 1$, whereas $a_0 p \exp(-f) \ll 1$, so that equation 20.24 could be reduced to

$$\theta = \frac{1}{f} \ln(a_0 p) \quad \dots (20.26)$$

which is referred to as the logarithmic Temkin isotherm, and shows that in the intermediate region the coverage θ is logarithmically related to p . For comparison the Langmuir isotherm can be written in the form

$$\ln \theta - \ln(1 - \theta) = \ln a_0 p \quad \dots (20.27)$$

showing that θ varies more slowly with increasing p in the Temkin isotherm than in the Langmuir isotherm, and that the larger the value of f the greater the divergence. Figure 20.14 illustrates Langmuir and Temkin isotherms, which show the variation of θ with pressure of the gas⁷.

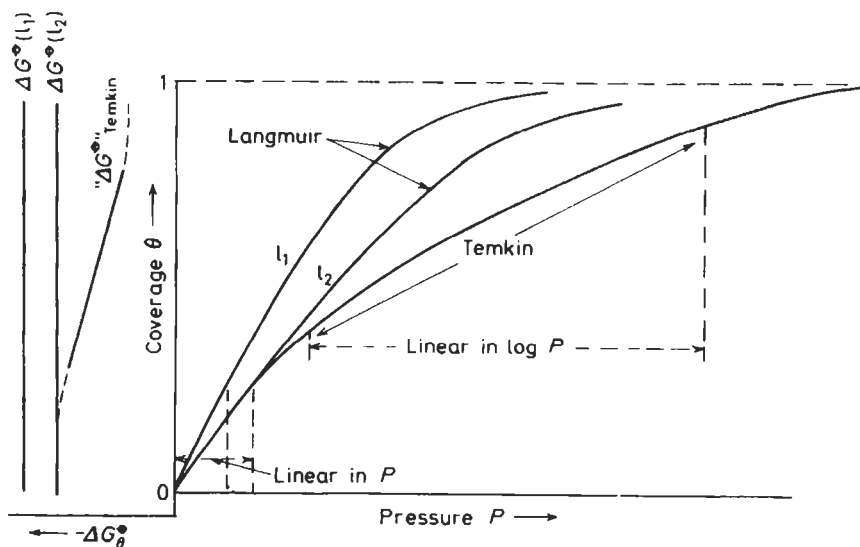


Fig. 20.14 Langmuir and Temkin isotherms showing variation of coverage as a function of pressure P of adsorbate. The Langmuir curves are for different Langmuir constants l_1 , and l_2 (a in equation 20.18), and the free energy of adsorption is assumed to be constant. In the Temkin isotherm coverage is linearly related to $\log P$ in the intermediate region owing to the variation of the free energy of adsorption with coverage (after Conway⁷)

Previous considerations have been confined to the effect of pressure and concentration upon coverage, but in an electrochemical equilibrium the activity and chemical potentials of the species adsorbing at the interface will also be a function of the potential difference $\Delta\phi$. For a solution containing unit activity of the species the effective pressure of the species at the interface is given by

$$p = \exp(\Delta\phi F/RT) \quad \dots (20.28)$$

and from equations 20.18 and 20.28

$$\frac{\theta}{1 - \theta} = a \exp(\Delta\phi F/RT) \quad \dots (20.29)$$

which shows how coverage is related to potential difference. The Langmuir and Temkin isotherms are of importance in relation to the adsorption of H on the metal during the hydrogen evolution reaction, in which the former is applicable at low coverages and the latter at high coverages.

Bockris, Devanathan and Muller¹⁰ (B.D.M.) in 1963 modified the Langmuir isotherm to take into account the dependence of the Langmuir constant (equation 20.19) on potential and coverage. The B.D.M. isotherm allows for the interaction of the adsorbed ions, which are assumed to be confined to the

I.H.P. and O.H.P. (the diffuse layer being disregarded), and a distinction is made between contact-adsorbed ions and ions electrostatically adsorbed by long-range coulombic forces. Wroblowa, Kovac and Bockris² showed that when $q_M = 0_{(p.z.c.)}$, the B.D.M. isotherm can be expressed in the form

$$\log a_{\pm} - \log \left(\frac{\theta}{1 - \theta} \right) = C + B\theta^{3/2} \quad \dots (20.30)$$

where a_{\pm} is the activity of the ion in solution and B and C are constants.

Thus a plot of $\left[\log a_{\pm} - \log \left(\frac{\theta}{1 - \theta} \right) \right]$ vs. $\theta^{3/2}$ should give a straight line of slope B and the intercept at $\theta = 0$ gives C . The B.D.M. isotherm has been found to show good agreement with the values actually obtained for the adsorption of various anions (Cl^- , CN^- , CNS^- , ClO_4^- , etc.) at a mercury electrode, and the constant C provides a means of evaluating the standard free energy of adsorption of an individual ion undergoing contact adsorption (chemical interaction) when $\theta \rightarrow 0$.

Adsorption in Corrosion Reactions

Some emphasis has been placed in this Section on the nature of the electrified interface since it is apparent that adsorption at the interface between the metal and solution is a precursor to the electrochemical reactions that constitute corrosion in aqueous solution. The majority of studies of adsorption have been carried out using a mercury electrode (determination of surface tension vs. potential, impedance vs. potential, etc.) and this has led to a greater understanding of the nature of the electrified interface and of the forces that are responsible for adsorption of anions and cations from solution. Unfortunately, it is more difficult to study adsorption on clean solid metal surfaces (e.g. platinum), and the situation is even more complicated when the surface of the metal is filmed with solid oxide. Nevertheless, information obtained with the mercury electrode can be used to provide a qualitative interpretation of adsorption phenomenon in the corrosion of metals, and in order to emphasise the importance of adsorption phenomena some examples are outlined below.

The adsorption theory of passivity¹¹ postulates that the phenomenon is due to the chemisorption of a monolayer of oxygen, which is considered to be atomic rather than molecular since the free energy of adsorption of O atoms usually exceeds the free energy for association of adsorbed molecular O_2 ; a second layer of O_2 molecules may chemisorb on top of the first monatomic layer, but is less energetically bound than the first. This adsorption is considered to interpose a stable barrier of O atoms and O_2 molecules between the metal and solution, displacing adsorbed H_2O and thus increasing the activation energy for dissolution of the metal lattice. Hoar¹² in presenting arguments in favour of the oxide film theory of passivity (see Section 1.5) points out that above the p.z.c. the adsorbed water dipoles will be oriented with the negative O^{2-} end of the dipole attached to the metal, and that above the reversible potential of $M + H_2O \rightarrow MO_{solid} + 2H^+ + 2e$ it will be kinetically easy for protons from the adsorbed water dipoles to

transfer to others adjacent to them in solution. The adsorbed O^{2-} ions are then taken up by the metal cations in the lattice to form a monolayer of solid oxide.

Adsorption is also of major importance in the breakdown of passivity by certain anions, and the fact that ions of small ionic diameter such as Cl^- and Br^- are conducive to breakdown was explained at one time in terms of their ability to penetrate the passive oxide; however, this view is not tenable since large anions (ClO_4^-) can cause breakdown, and there is little evidence of the presence of pre-existing pores in the film. Irrespective of the mechanism of penetration, it is evident that it must be preceded by replacement of the adsorbed water by adsorbed anions, which will be favoured by a high anion concentration and by a higher (more positive) interfacial potential difference between the oxide film on the metal and the solution. Hoar¹² points out that as anion adsorption by replacing adsorbed water dipoles proceeds, the interfacial tension (or interfacial free energy) of the oxide/solution interface is progressively lowered by the mutually repulsive forces between adsorbed anions in a similar way to that of the mercury in the Lippmann electrometer. Eventually, the interfacial tension is lowered sufficiently for a kind of peptisation of the oxide by the interfacial charge to occur, and the adsorbed anions push one another, and the oxide to which they are strongly attached, apart thus resulting in a crack or split in the protective film.

Adsorption is, of course, of major importance in the inhibition of corrosion by organic compounds (adsorption inhibitors) that have the ability to adsorb strongly on the metal surface, thus impeding the dissolution reaction and reducing the corrosion rate. It follows that the coverage of a metal surface by adsorbed inhibitor can be evaluated from the relationship

$$\theta = 1 - \frac{k_i}{k}$$

where k_i and k are the corrosion rates in solutions with and without the inhibitor, respectively. The variation in coverage with concentration of inhibitor frequently conforms with Frumkin's isotherm^{13,14}

$$\frac{\theta}{1 - \theta} \exp(f\theta) = Kc$$

where K is the equilibrium constant for the adsorption reaction, c is the concentration of the inhibitor and f is a parameter connected with the variation of adsorption energy with θ which is positive when the free energy of adsorption decreases with coverage, and negative when it increases

$$\Delta G_a = \Delta G^\circ + fRT\theta$$

The Frumkin isotherm can be regarded as a general isotherm from which both the Temkin and Langmuir isotherms can be obtained as special cases. Szklarska-Smialowski and Wieczorek¹⁵ found that the adsorption of various aliphatic compounds (acids, alcohols and amines) on steel in H_2SO_4 conformed with the Frumkin isotherm.

In connection with the adsorption of organic molecules at the surface of an electrode it is possible to distinguish two types: (a) adsorption of undissociated molecules and (b) adsorption of intermediates formed by dissociation of the original molecule. The variation of coverage of the surface of a

mercury electrode with undissociated organic molecules with potential frequency takes a parabolic form with θ attaining a maximum at potentials close to the p.z.c., and this can be explained in terms of competitive adsorption between the molecules and water dipoles. Although the water dipoles are strongly attracted to the electrode at potentials more negative or more positive than the p.z.c. (Fig. 20.3), they are only weakly held at potentials close to the p.z.c., at which $\theta_{\text{H}_2\text{O}}$ obtains a minimum value, and the organic molecules have the greatest chance of displacing adsorbed water and becoming adsorbed themselves. The mechanism of the adsorption of organic inhibitors is outside the scope of this section, and reference should be made to Section 17.3 and to the comprehensive review by TrabANELLI and Carassiti¹⁶.

Electrode Kinetics

Homogeneous Chemical Reactions

Before considering the velocity (the kinetics) of an electrochemical reaction in which charge transfer takes place at a metal/solution interface, it is relevant to consider briefly the kinetics of homogeneous chemical reactions. The rate of homogeneous chemical reaction will depend on a variety of factors of which concentration of reactants, temperature, radiation and catalysis are the most important, and will range from almost instantaneous (neutralisation of a strong acid by a strong base) to extremely slow (reaction of H_2 , and O_2 at ambient temperatures to form water). In a number of systems, although there is a high thermodynamic tendency for the reaction to proceed, it is nullified by kinetic factors so that the reaction proceeds extremely slowly, and many corrosion reactions fall into this category.

The rate of a chemical reaction is proportional to the concentration of the reactants, and for a reversible isothermal homogeneous reaction:



the rate of the forward reaction \vec{v} will be

$$\vec{v} = \vec{k} c_A^a c_B^b \quad \dots (20.32)$$

and the rate of the reverse reaction will be

$$\overleftarrow{v} = \overleftarrow{k} c_C^c c_D^d \quad \dots (20.33)$$

where \vec{k} and \overleftarrow{k} are the rate constants for the forward and reverse reactions, respectively. Since the rates are dependent on the concentration of the species involved in the reaction, it follows that the rate of the forward reaction will decrease whilst that of the reverse reaction will increase as the reaction progresses. Finally, the velocities will become equal and a state of dynamic equilibrium will be attained

$$\vec{v} = \overleftarrow{v} \quad \text{and} \quad \vec{k} c_A^a c_B^b = \overleftarrow{k} c_C^c c_D^d \quad \dots (20.34)$$

and the concentrations of the reactants and products are now the equilibrium values at the temperature under consideration. Therefore

$$\frac{c_C^c c_D^d}{c_A^a c_B^b} = \frac{\vec{k}}{\overleftarrow{k}} = K \quad (20.34a)$$

where K is the equilibrium constant for the reaction at a given constant temperature, and K will increase or decrease with increase in temperature according to the variation of ΔG^θ with temperature ($\Delta G^\theta = -RT \ln K$). Thus

for equilibria of the type $2\frac{x}{y}M + O_2 = \frac{2}{y}M_xO_y$, K decreases with increase in temperature so that p_{O_2} increases, whereas in the case of the equilibrium $2C + O_2 = 2CO$ the converse applies and K increases (see Section 7.6, Fig. 7.56).

The dependence of the velocity of a reaction on concentration follows from the fact that the forces between the molecules are of short range so that reaction will take place only when the reactant molecules are almost in contact. Thus 'collision' of two (or more) molecules must occur for reaction to take place, and since the probability of the two reacting molecules being in a specific place is proportional to the product of their concentrations, the rate of reaction will be proportional to the concentrations of the reactants.

Increase in temperature increases velocity, and for a homogeneous process the rate constant k increases by ≈ 200 to 300% for each 10 K increase in temperature, which is surprisingly high, since the number of collisions between molecules increases by only approximately 2% per 10 K increase in temperature. This anomaly was resolved by Arrhenius who suggested that in every system an equilibrium exists between 'normal' and 'active' molecules, and that it is only the latter that have sufficient energy to participate in the reaction, although the collisions of these active molecules represents only a small proportion of the total collisions. At a given constant temperature the active molecules are a constant fraction of the total number so that the theory is not inconsistent with the fact that the reaction rate is proportional to the concentration of the total molecules. Thus for a molecule to react its kinetic energy must be sufficiently greater than the average kinetic energy at that temperature to enable it to climb to the top of the energy barrier; molecules possessing this energy (or more) are said to be *activated* and the energy E^* to surmount the barrier is the *activation energy* of the reaction (units of J mol^{-1}).

The number of molecules n_E possessing an energy in excess of a given value of kinetic energy E is given by Maxwell's Distribution Law

$$n_E = n \exp(-E/RT) \quad \dots (20.35)$$

where n is the total of the molecules. It follows that a similar relationship will apply between the chemical rate constant and the height of the energy barrier E^* that only the activated molecules are able to surmount

$$k_{\text{chem.}} = A \exp(-E^*/RT) \quad \dots (20.36)$$

where A is a constant and $k_{\text{chem.}}$ is the chemical rate constant.

Equation 9.36 is referred to as the Arrhenius equation, and taking logarithms

$$\ln k_{\text{chem.}} = \ln A - \frac{E^*}{RT} \quad \dots (20.37)$$

or

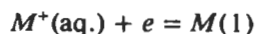
$$2.3 \log k_{\text{chem.}} = 2.3 \log A - \frac{E^*}{RT} \quad \dots (20.38)$$

Thus a plot (Arrhenius plot) of $\log k_{\text{chem.}}$ against $1/T$ will give a straight line of slope $-E^*/2.3 R$, which enables the activation energy to be evaluated from the variation of the rate constant with temperature. Equation 20.38 shows that the smaller the activation energy of a reaction (the lower the height of the energy barrier) the more rapid the reaction at a given temperature, and that for any reaction the rate of reaction will increase with increase in temperature.

Rate of Electrochemical Reaction

Previous considerations have shown that in homogeneous chemical reactions the rate is determined by the concentrations of reactants and the temperature, and that under the same conditions of concentration and temperature different reactions will proceed at rates that vary according to the activation energies of the reaction. Similar considerations to the above apply to heterogeneous reactions involving charge transfer at a metal/solution interface, but the potential of the electrified interface introduces an important additional factor, and the reactant rate at constant temperature and concentration of reactants can be increased or decreased very significantly by changing the potential of the electrified interface.

Consider the cathodic reduction of a hydrated metal ion $M^+(\text{aq.})$ to a lattice metal atom at the interface $M/M^+(\text{aq.})$ by a simple one-step reaction



which has been selected to avoid the complications that are involved when the overall reaction consists of two or more steps of which one is slower than the other and is thus rate determining² (see p. 20.43).

In the double layer the ion will be hydrated and its distance from the metal surface will be approximately the diameter of the water molecule attached to the metal surface plus the radius of the hydrated metal ion, i.e. $0.28 + (\frac{1}{2} \times 2.8) + r_{M^+} \approx 0.5-0.6 \text{ nm}$ which is the distance between the metal surface and the O.H.P. The ion will be vibrating constantly with respect to its hydration sheath, and in its attempt to attain the metal surface it will have to surmount the energy barrier (Fig. 20.15), which is regarded as having a maximum potential energy at a distance approximately half-way between its original position at the O.H.P. and the metal surface. At this maximum the metal ion receives the electron and becomes an uncharged atom, which can then descend of its own accord along the remainder of the potential energy-distance (Morse) curve and enter the lattice of the metal. It also follows that only metal ions with an energy greater than the maximum

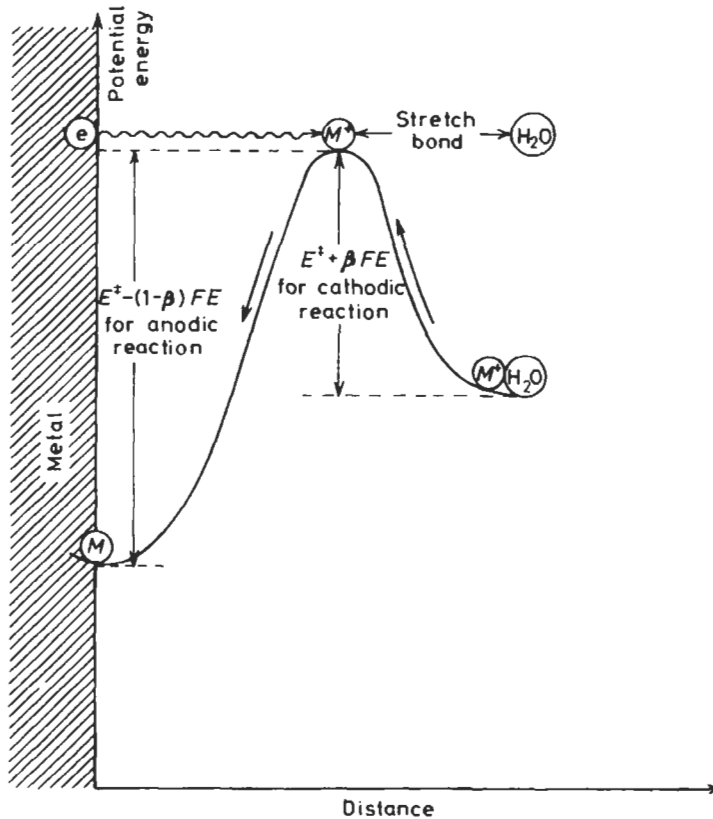


Fig. 20.15 Cathodic reduction of $M^+(\text{aq.})$ to metal in which the activation energy (height of the energy barrier) for the cathodic reaction is lowered to $E^\ddagger + \beta FE$ whilst that for the anodic reaction is raised to $E^\ddagger - (1 - \beta) FE$ (note that E^\ddagger is positive and E negative). (After Bockris and Drazic²)

will be able to surmount the potential energy barrier and become metal atoms. Fig. 20.15 shows how the rate of a cathodic reaction can be increased by changing the height of the energy barrier (cf. Fig. 20.16*b* for the electrode at equilibrium). Potential energy *vs.* distance curves and corresponding potential differences for the various possibilities at an electrified interface are shown in Fig. 20.16. If the reaction was independent of the potential, as it would be if there was no excess charge and the potential was $E_{p.z.c.}$ (Fig. 20.16*a*), the rate would conform to a first-order chemical reaction (the order of a reaction is the number of atoms or molecules whose concentration determines the velocity), and

$$v_{\text{chem.}} = k_{\text{chem.}} c_{M^+(\text{aq.})} \quad \dots (20.39)$$

in which $k_{\text{chem.}}$ is defined by equation 20.36; under these conditions the rate will be proportional to $c_{M^+(\text{aq.})}$. However, in the case of an electrochemical reaction the rate will also depend on the potential difference at the interface.

If the potential of the metal/solution interface is made more negative than $E_{p.z.c.}$ by giving it an excess negative charge the positively charged ion will

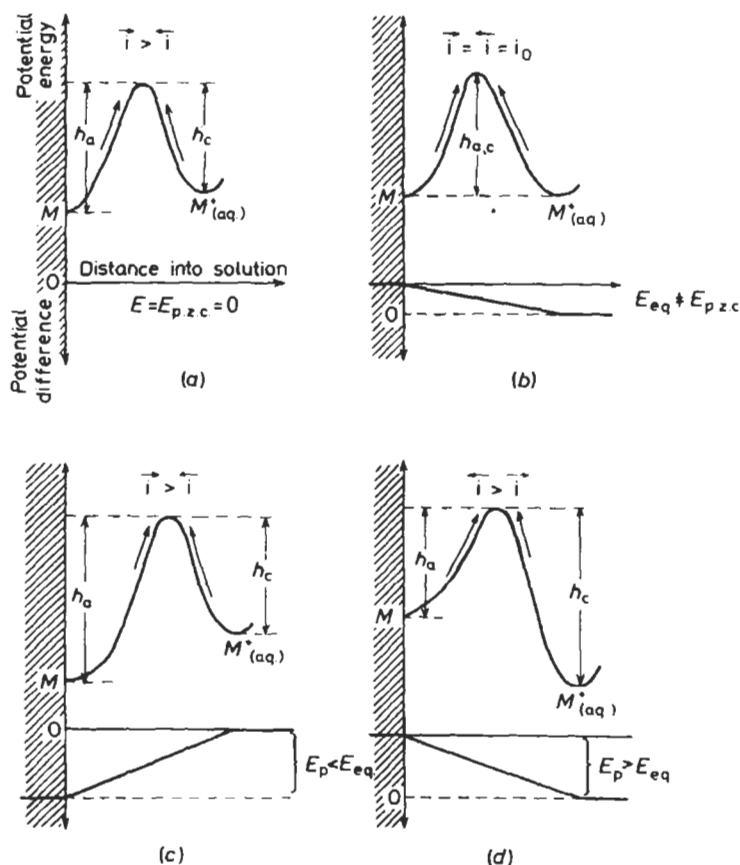


Fig. 20.16 Potential energy against distance curves (Morse curves). (a) No potential difference (p.z.c.), (b) at the equilibrium potential when $i_c = i_a$ and the heights of the energy barrier are the same for both reactions, but $E_{eq} \neq E_{p.z.c.}$, (c) potential made more negative than E_{eq} , and (d) potential made more positive than E_{eq} . The p.z.c. has been taken as zero potential, and h_a and h_c are the heights of the potential barriers for the anodic and cathodic reactions, respectively; i_c is the rate of the cathodic reaction and i_a the rate of the anodic reaction (after Bockris and Drazic²)

be electrostatically attracted to the metal, and this will result in an increase in the rate of the cathodic reaction and a decrease in the rate of the anodic reaction which are equal only at E_{eq} , i.e. the height of the energy barrier for cathodic reduction will be lowered whilst that for anodic dissolution will increase (Fig. 20.17). The chemical rate equation must now be modified to take into account the energy associated with the passage of $1F$ coulombs of charge (for 1 mol of M^+ , or zF coulombs for 1 mol of M^{z+}) through a potential difference E , i.e. $EFJ \text{ mol}^{-1}$. However, all this energy is not required since once the metal ion has been given sufficient energy to attain the energy hump it will move down the other side on its own accord. Hence the energy required will be xEF where $x < 1$. If δ is the distance between

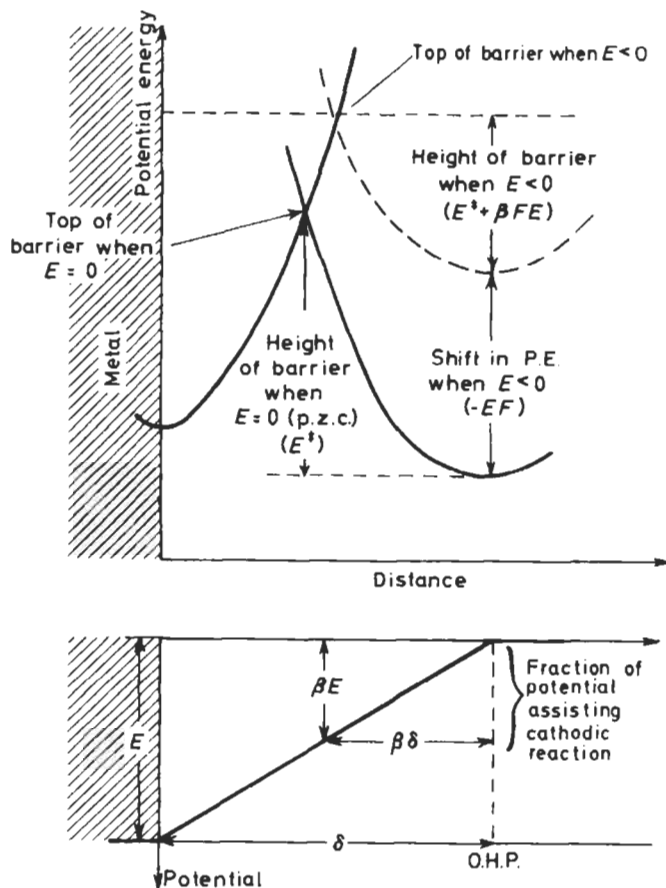


Fig. 20.17 Potential energy-distance curves for a cathodic reaction showing how the potential energy barrier is lowered by βFE when $E < E_{p.z.c.}$. The barrier is assumed to be symmetrical so that $\beta \approx \frac{1}{2}$, where δ is the distance of the O.H.P. from the surface of the electrode. Full curve—no field across double layer; dashed curve—potential difference is E and is negative

I.H.P. and O.H.P., and if the energy barrier is assumed to be symmetrical, then the energy hump. will be at $\frac{1}{2}\delta$. If β is the *symmetry factor* ($\beta \approx \frac{1}{2}$), the electrochemical rate equation can be written

$$\vec{k}_c = A \exp \left[- (E^* + \beta EF) / RT \right] \quad \dots (20.40)$$

and from equation 20.36

$$\vec{k}_c = \vec{k}_{chem.} \exp(-\beta EF / RT) \quad \dots (20.41)$$

where \vec{k}_c is the electrochemical rate constant and $\vec{k}_{chem.}$ the chemical rate constant for the cathodic reaction, and is the symmetry factor.

$$\therefore \vec{v}_c = \vec{k}_c c_i = \vec{k}_{chem.} \exp(-\beta EF / RT) c_i \quad \text{mol cm}^{-2} \text{ s}^{-1} \quad \dots (20.42)$$

and since
$$v = \frac{i}{F} \text{ mol cm}^{-2} \text{ s}^{-1} \quad \dots (20.43)$$

where i is the current density (A cm^{-2})

$$\vec{i} = F\vec{k}_e \exp(-\beta EF/RT) c_i \text{ A cm}^{-2} \quad \dots (20.44)$$

which shows that the rate of an electrochemical cathodic reaction increases exponentially as E becomes more negative.

Since for the cathodic process the fraction of the energy was βEF it is reasonable to assume that when the ion travels in the reverse direction during an anodic process the fraction of the energy will be $(1 - \beta)EF$. Thus for the anodic process

$$\vec{v}_e = \vec{k}_{\text{chem.}} \exp[(1 - \beta)EF/RT] \quad \dots (20.45)$$

and the rate will increase as E becomes more positive. Also

$$\vec{i} = Fk_{\text{chem.}} \exp[(1 - \beta)EF/RT] \quad \dots (20.46)$$

in which there is no concentration term since the activity of a pure metal is invariant and equals unity (cf. equation 20.44).

Generalising, for a reaction involving M_{z+} , for a cathodic reaction

$$\vec{i} = zF\vec{k}_{\text{chem.}} c_i \exp(-\beta EF/RT) \text{ A cm}^{-2} \quad \dots (20.47)$$

and for an anodic reaction

$$\vec{i} = zF\vec{k}_{\text{chem.}} \exp[(1 - \beta)EF/RT] \text{ A cm}^{-2} \quad \dots (20.48)$$

Overpotential

When an electrode is at equilibrium the rate per unit area of the cathodic reaction equals that of the anodic reaction (the partial currents) and there is no *net* transfer of charge; the potential of the electrode is the equilibrium potential and it is said to be unpolarised:

$$\vec{i} = \vec{i} = i_0 \quad \dots (20.49)$$

where i_0 is the equilibrium exchange current density, and

$$E = E_{\text{eq.}}, \text{ and } \eta = E - E_{\text{eq.}} = 0 \quad \dots (20.50)$$

Thus η the *overpotential* is defined as the departure of the potential of the electrode from its equilibrium value.

For a cathodic process in which the electrode is polarised to a potential E_p

$$\vec{i} > \vec{i} \text{ and } i_c = \vec{i} - \vec{i} \quad \dots (20.51)$$

where i_c is the *net* cathodic current density that results when E_p is made more negative than the equilibrium potential $E_{\text{eq.}}$. By definition

$$\eta_c = E_{p,c} - E_{\text{eq.,c}} \quad \dots (20.52)$$

and since for a cathodic reaction

$$E_{p,c} < E_{eq.,c}$$

then $\eta_c < 0$, i.e. it is always negative. Similarly, for a net anodic process

$$\vec{i} > \vec{i}^- \text{ and } i_a = \vec{i}^- - \vec{i} \quad \dots (20.53)$$

and

$$\eta_a = E_{p,a} - E_{eq.,a} \quad \dots (20.54)$$

and since

$$E_{p,a} > E_{eq.}$$

then $\eta_a > 0$, i.e. it is always positive.

At equilibrium, \vec{i}^- and \vec{i} in equations 20.44 and 20.46 can be replaced by i_0 and the E s by $E_{eq.}$

$$\therefore i_0 = zF\vec{k}_c \exp[(1 - \beta)E_{eq.}F/RT] = zF\vec{k}_c \exp(-\beta E_{eq.}F/RT) \quad \dots (20.55)$$

If the reaction is proceeding at a finite rate, the E s will be the polarised potentials E_p , and since

$$E_p = \eta_a + E_{eq.} \quad \dots (20.56)$$

equation 20.46 can be expressed as

$$\vec{i}^- = zF\vec{k}_c \exp[(1 - \beta)E_{eq.}F/RT] \exp[(1 - \beta)\eta_a F/RT] \quad \dots (20.57)$$

and from equation 20.55 for an anodic process

$$\vec{i}^- = i_0 \exp[(1 - \beta)\eta_a F/RT] \quad \dots (20.58)$$

Similarly for the cathodic process

$$\vec{i} = i_0 \exp(-\beta\eta_c F/RT) \quad \dots (20.59)$$

and in both cases the greater the magnitudes of i_0 and η (taking into account the appropriate sign) the greater the rate per unit area of the reaction.

The net current density is the difference between the two partial current densities, and the net anodic current density can be written in the form

$$i_a = \vec{i}^- - \vec{i} \quad \dots (20.60)$$

(the net current density can be cathodic or anodic, and the above equation could be written in the form $i_c = \vec{i} - \vec{i}^-$ without affecting the argument). Introducing equations 20.58 and 20.59 into equation 20.60

$$i_a = i_0 [\exp[(1 - \beta)\eta_a F/RT] - \exp(-\beta\eta_a F/RT)] \quad \dots (20.61)$$

It can be seen that when $\eta = 0$, $i = i_0$ and the rate of the cathodic process equals that of the anodic process, i.e. the reaction is at equilibrium. However, if η is positive the first term increases exponentially, whilst the second term decreases exponentially, and at overpotentials $> +0.052$ V the

latter can be neglected. Thus at overpotentials $> +0.052$ V equation 20.61 simplifies to

$$i_a = i_0 \exp[(1 - \beta)\eta_a F/RT] \quad \dots (20.62)$$

Similarly, for overpotentials more negative than -0.052 V the first term becomes negligible, and

$$i_c = -i_0 \exp(-\beta\eta_c F/RT) \quad \dots (20.63)$$

Taking logarithms in equation 20.62

$$\ln i_a = \ln i_0 + \frac{(1 - \beta)\eta_a F}{RT} \quad \dots (20.64)$$

and for the anodic reaction

$$\eta_a = \frac{-RT}{(1 - \beta)F} \ln i_0 + \frac{RT}{(1 - \beta)F} \ln i \quad \dots (20.65)$$

and since

$$\begin{aligned} \frac{RT}{F} \ln x &= 0.059 \log x \text{ at } 25^\circ\text{C, then} \\ \eta_a &= \frac{-0.059}{(1 - \beta)} \log i_0 + \frac{0.059}{(1 - \beta)} \log i \quad \dots (20.66) \end{aligned}$$

Similarly for the cathodic reaction

$$\eta_c = \frac{+0.059}{\beta} \log i_0 - \frac{0.059}{\beta} \log i \quad \dots (20.67)$$

which was obtained first by Tafel from experimental studies of the hydrogen evolution reaction on various metals, and was expressed in the form

$$\eta = a + b \log i \text{ (Tafel equation)} \quad \dots (20.68)$$

Attention should be drawn to the signs in equations 20.66 and 20.67 and it should be noted that the Tafel slope b is always positive for an anodic process and negative for a cathodic process and that the constant a is of opposite sign to the slope.

The most significant parameter in the relationships given above is the equilibrium exchange current density i_0 , which can be evaluated by extrapolating the linear η vs. $\log i$ curve to $\eta = 0$, at which $\log i = \log i_0$. Alternatively, i_0 may be evaluated from the linear E_p vs. $\log i$ curve by extrapolating the curve to the equilibrium potential E_{eq} .

There are two further possibilities that must be considered, and these are discussed below.

Multistep reactions Previous considerations have been based on a simple one-step reaction involving one electron, but if the reaction occurs by a series of steps of which one is significantly slower than all the others, which may be regarded as at equilibrium, and is thus rate determining, equation 20.61 is not valid and becomes

$$i_a = i_0 [\exp \overleftarrow{\alpha} \eta_a F/RT - \exp \overrightarrow{\alpha} \eta_a F/RT] \quad \dots (20.69)$$

where $(1 - \beta)$ is replaced by α the transfer coefficient for the anodic reaction, and β is replaced by α the transfer coefficient for the cathodic reaction. Neglecting the second term, as in equation 20.62, and expressing equation 20.62 in terms of overpotential

$$\eta_a = -\frac{0.059}{\alpha} \log i_0 + \frac{0.059}{\alpha} \log i_a \quad \dots (20.70)$$

The parameters included in the transfer coefficient will be considered subsequently in relation to the r.d.s. of the hydrogen evolution reaction.

Small overpotentials For overpotentials < 0.010 V, equation 20.61 can be simplified using the identity

$$e^x = 1 + x + \frac{x^2}{2!} + \dots \text{ and } e^{-x} = 1 - x + \frac{x^2}{2!} - \dots$$

and, taking only the first two terms

$$i = i_0 \left[\left(1 + \frac{(1 - \beta)F\eta}{RT} \right) - \left(1 - \frac{\beta F\eta}{RT} \right) \right] \quad \dots (20.71)$$

which reduces to

$$i = \frac{i_0 F}{RT} \times \eta, \text{ or } \eta = \frac{RT}{i_0 F} \times i \quad \dots (20.72)$$

showing that η against i is linear with a slope of $RT/i_0 F$. Equation 20.72 is applicable to either the anodic or the cathodic reaction, and provides another method of evaluating i_0 .

Transport or Concentration Overpotential

Transport of a species in solution to and from an electrode/solution interface may occur by migration, diffusion and convection although in any specific system they will not necessarily be of equal importance. However, at the steady state all steps involved in the electrode reaction must proceed at the same rate, irrespective of whether the rate is controlled by a slow step in the charge transfer process or by the rate of transport to or from the electrode surface. It follows that the rate of transport must equal the rate of charge transfer:

$$J = \frac{dQ}{dt} = \frac{i}{zF} \quad \dots (20.73)$$

where J the transport flux equals the number of moles transported across an area of $1 \text{ cm}^2/\text{s}$ (dQ/dt) and i is the charge transfer per unit area of surface (A cm^{-2}).

In a cathodic process, removal of ions from solutions will result in a decrease in their concentration at the electrode/solution interface compared to that in the bulk solution, and this in turn will cause a concentration gradient and consequent diffusion. Furthermore, the potential gradient

through the solution will result in the migration of cations and anions to their respective electrodes (electrolytic conduction), although it does not follow that the ion transported to the electrode surface by migration will necessarily participate in the reaction. Thus copper can be cathodically deposited from a sulphuric acid plus copper sulphate solution at 100% cathode efficiency, but charge transport through the solution will be predominantly by H_3O^+ ions, the Cu^{2+} ions being transported to the electrode surface mainly by diffusion. On the other hand, in a concentrated solution of aluminium sulphate, charge transport through the solution will be mainly due to migration of Al^{3+} and SO_4^{2-} , but the electrode process at the cathode will be solely hydrogen discharge. In the case of a cathodic process involving an uncharged species such as dissolved oxygen, transport is solely by diffusion and other ions in solution will be responsible for migration. In addition to diffusion and migration, ions and uncharged species may be transported to the electrode surface either by convection resulting from density differences within the solution caused by uneven heating or cooling of the solution, or by the electrode process itself. Thus during the heating of a solution contained in a beaker, the hot solution of the bottom of the beaker will tend to rise because of its decreased density, whilst the cold solution at the top will tend to fall. Even when a solution is not deliberately heated, evaporation from the surface or air draughts may give rise to temperature differences and hence convective mixing; indeed it is extremely difficult to avoid convective mixing and for this reason solutions used in corrosion testing are often stirred in order to obtain reproducible conditions.

Forced convection can be achieved in a variety of ways, e.g. by agitating the solution (stirring mechanically, sparging with gas bubbles, ultrasonic radiation, etc.) or by moving or rotating the metal electrode, and this will result in more rapid transport of the reacting species to the electrode than when the solution is unagitated.

Diffusion and Transport Overpotential (η_T)

When a cathodic process occurs at a finite rate the concentration $c_{x=0}$ of the electron acceptor (cathode reactant) at the metal/solution interface ($x = 0$) will become less than that in the bulk solution c_b , and as the rate increases it will continue to decrease until it becomes zero, i.e. as soon as the electron acceptor arrives at the interface electron transfer occurs.

Thus for a cathodic process

$$c_{x=0} < c_b, \text{ and } E_{x=0} < E_b$$

whereas for the anodic process

$$c_{x=0} > c_b, \text{ and } E_{x=0} > E_b$$

Thus owing to the electrode process the potential will change and will become more negative in a cathodic process and more positive in an anodic process:

$$E_{c,x=0} < E_b < E_{a,x=0}$$

where E_b is the potential of the metal in the bulk solution.

If the system is regarded as a reversible concentration cell, the Nernst

equation can be applied (Section 20.2, equation 20.187) and the transport overpotential η_T for a cathodic process is given by

$$\eta_T = E_{x=0} - E_b = \frac{RT}{zF} \ln \left(\frac{c_{x=0}}{c_b} \right) = \frac{0.059}{z} \log \left(\frac{c_{x=0}}{c_b} \right) \text{ at } 25^\circ\text{C} \quad \dots (20.74)$$

and since $c_{x=0} < c_b$, η_c will be negative; the converse will apply to an anodic process and η_a will be positive. Although c_b is known, the concentration at the interface $c_{x=0}$ is unknown and cannot be readily determined experimentally. However, if it is assumed that there is a stagnant layer of solution adjacent to the electrode through which transport occurs entirely by diffusion, it is possible to evaluate $c_{x=0}$ from diffusion theory. For simplicity, this layer is regarded as having a precise thickness δ and a linear concentration gradient, although non-linearity occurs at the outer plane of the layer where the gradient becomes asymptotic (Fig. 20.18). The thickness, however, varies according to conditions and will depend on the geometry of the electrode, the diffusion coefficient of the reacting species, and the kinematic viscosity (density/viscosity) and velocity of the solution. Under steady-state conditions of natural convection, $\delta \approx 0.05$ cm but it decreases under conditions of high forced convection to a value of ≈ 0.001 cm, and even lower values

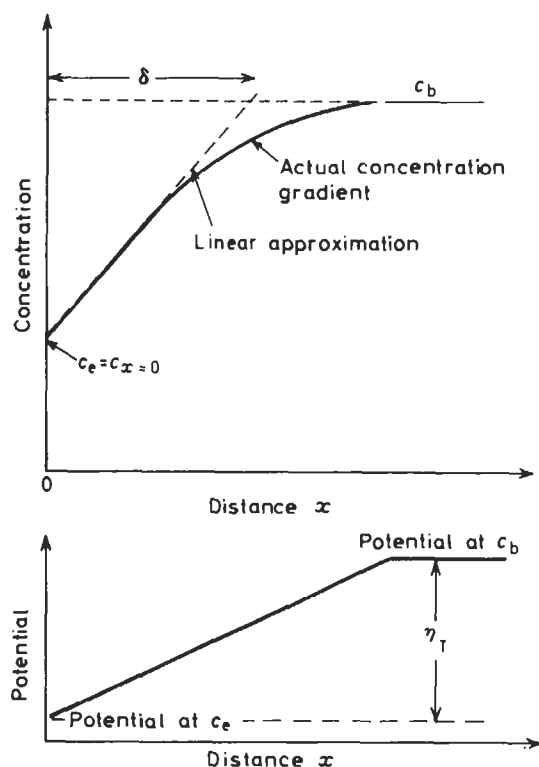


Fig. 20.18 Concentration gradient and potential gradient in the diffusion layer for a cathodic process (note that the potential drop through the solution has not been included)

may be obtained under conditions of very rapid laminar flow such as is produced by a rotating-disc electrode.

If it is assumed that transport is entirely by diffusion and that there is a linear concentration gradient through the diffusion layer, the concentration gradient at $x = 0$, i.e. $(dc/dx)_{x=0}$, can be expressed as $(c_b - c_{x=0})/\delta$. From Fick's first law and equating the transport flux J with the rate i of an electrochemical reaction

$$J = -D \frac{dc}{dx} = -D \frac{(c_b - c_{x=0})}{\delta} = \frac{i}{zF} \quad \dots (20.75)$$

where D is the diffusion coefficient

$$\therefore i = -DzF \times \frac{(c_b - c_{x=0})}{\delta} \quad \dots (20.76)$$

The concentration gradient will be a maximum when $c_{x=0} = 0$, and this will correspond with the *maximum* or *limiting* current density i_L

$$\therefore i_L = \frac{-DzFc_b}{\delta} \quad \dots (20.77)$$

The Nernst equation written in terms of the transport overpotential of a cathode is

$$\eta_T = \frac{RT}{zF} \ln \frac{c_{x=0}}{c_b} \quad \dots (20.78)$$

and from equation 20.76

$$c_b - c_{x=0} = -\frac{\delta}{DzF} \times i, \text{ or } \frac{c_{x=0}}{c_b} = 1 + \frac{\delta}{DzFc_b} \times i \quad \dots (20.79)$$

From equation 20.77

$$\frac{\delta}{DzFc_b} = -\frac{1}{i_L} \quad \dots (20.80)$$

hence from equations 20.79 and 20.80

$$\frac{c_{x=0}}{c_b} = 1 - \frac{i}{i_L} \quad \dots (20.81)$$

Substituting in equation 20.78

$$\eta_T = \frac{RT}{zF} \left(1 - \frac{i}{i_L} \right) \quad \dots (20.82)$$

which gives the relationship between η_T and i for a cathodic reaction in which the overpotential is solely due to transport. In Fick's law (equation 20.75) the minus sign is introduced since the x direction is taken to coincide with the direction at which diffusion occurs and $\delta c/\delta x$ is therefore negative. The negative sign can however be neglected in calculating i_L from equation 20.77.

The limiting current density in equation 20.77 has been derived on the assumption that transport is solely by diffusion, but if migration also occurs then for a cathodic process

$$i_L = \frac{DzFc_b}{\delta(1 - n_+)} \quad \dots (20.83)$$

where n_+ is the transference number of the cation that is involved in charge transfer. In this equation i_L is in $A\ cm^{-2}$, D is in $cm^2\ s^{-1}$ and c_b is in $mol\ cm^{-3}$ or $g\ ions\ cm^{-3}$ (the r.h.s. of equation 20.83 must be multiplied by 10^{-3} if c_b is in $mol\ dm^{-3}$). It should be noted that equation 20.83 involves 1 mol of the reactant and z must be evaluated accordingly, i.e. for the hydrogen evolution reaction (h.e.r.) $H^+ (1\ mol) + e = \frac{1}{2}H_2$ and $z = 1$; for the oxygen-reduction reaction, $O_2 (1\ mol) + 2H_2O + 4e = 4OH^-$, and $z = 4$.

For the majority of ions the diffusion coefficient D is $\approx 10^{-5}\ cm^2\ s^{-1}$ at 25° (the values of H^+ and OH^- at infinite dilution are somewhat higher, i.e. $9.3 \times 10^{-5}\ cm^2\ s^{-1}$ and $5.2 \times 10^{-5}\ cm^2\ s^{-1}$, respectively) so that equation 20.83 can be simplified:

$$i_L \approx \frac{10^{-5} \times 96\ 500 z c_b}{0.05} \approx 2 \times 10^1 z c_b \quad (\text{for natural convection})$$

$$i_L \approx \frac{10^{-5} \times 96\ 500 z c_b}{0.001} \approx 1 \times 10^3 z c_b \quad (\text{for extreme forced convection})$$

where i_L is in $A\ cm^{-2}$ and c_b is in $mol\ cm^{-3}$, which represents the two extremes of i_L . Thus i_L can be increased by increasing c_b the bulk concentration, and by decreasing the thickness of the diffusion layer by forced convection. It should also be noted that D increases with temperature ($\approx 2\text{--}3\%/^\circ C$ rise) and i_L will therefore increase with temperature.

From the identity $\ln(1 - x) = x - \frac{1}{2}x^2 + \frac{1}{3}x^3$ it is evident that $\ln(1 - x) \rightarrow x$ for small values of x . Thus for small values of i , equation 20.82 can be written

$$\eta_T = \frac{0.059}{z} \frac{i}{i_L} = \frac{k}{z} \times i \quad \dots (20.84)$$

and η will be linearly related to i . At higher current densities the curve departs from linearity, and as $i \rightarrow i_L$, $\eta_c \rightarrow \infty$ and becomes infinitely negative, and the rate of the process remains constant at i_L . Any further increase in rate will then require an alternative charge transfer process.

Since in most cases of corrosion in which transport of the cathodic reactant (H_3O^+ , dissolved O_2 , Fe^{3+} , HNO_3 acid, etc.) is rate determined, the anodic curve intersects the cathodic curve at i_L , then

$$i_L = i_{corr.} \quad \dots (20.85)$$

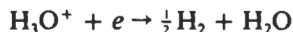
and any factor that increases i_L will result in a corresponding increase in $i_{corr.}$

The Hydrogen Evolution Reaction

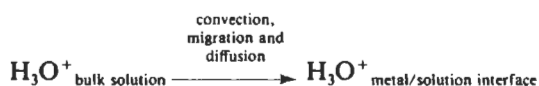
The hydrogen evolution reaction (h.e.r.) is of particular importance in corrosion for a number of reasons. Firstly, the reduction of the H_3O^+ ion in acid solutions or the H_2O molecule in neutral and alkaline solution is a common cathodic reaction for the corrosion of metals in acid, neutral and alkaline solutions; the fact that iron will corrode in neutral water free from dissolved

oxygen with the evolution of H_2 can be confirmed by testing the gas bled off from the radiator of a central-heating system. Secondly, hydrogen may pass into the lattice of certain metals and lead to embrittlement (*see* Section 8.4), and in the case of a number of alloys, particularly the high-tensile steels, it can lead to a catastrophic fracture. The h.e.r. has been the most widely studied electrode reaction, and some account of its complexity can be gained from the short account that follows.

In deriving the kinetics of activation-energy controlled charge transfer it was emphasised that a simple one-step electron-transfer process would be considered to eliminate the complications that arise in multistep reactions. The h.e.r. in acid solutions can be represented by the overall equation:



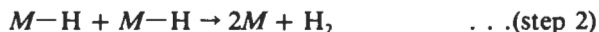
and at first sight it would appear that this reaction was as simple as $M_{(aq)}^+ + e \rightarrow M$. However, this is not the case and the sequence of events can be expressed by the following reactions:



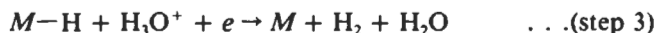
discharge step (D.)



followed by *either* a chemical desorption (C.D.) step



or, an electrochemical desorption (E.D.) step



It should be noted that the terminology used is variable and that step 2 is also referred to as 'combination', 'recombination' and 'Tafel combination'; step 3 is also referred to as 'ion-atom desorption'.

A similar series of steps can be written for the h.e.r. in neutral and alkaline solutions, but the equations will then involve the water molecule, since the concentration of H_3O^+ in these solutions is too small for it to participate at a significant reaction rate.

It is important to note that the discharge step involves adsorption of hydrogen atoms at available sites on the metal surface, and is followed by desorption that may be either a chemical step (step 2), or an electrochemical step (step 3) in which further charge transfer occurs. The extent of adsorption of hydrogen atoms is referred to as coverage θ , and $\theta_H = 1$ represents coverage of all the sites available with adsorbed hydrogen atoms; coverage will vary with the mechanism of the h.e.r., the overpotential, the nature of the metal, the nature of the solution, etc.

After adsorption the H_{ads} may be removed as H_2 molecules by either step 2 or 3, but as mentioned above there is an additional step:



which represents the transfer of the $H_{\text{ads.}}$ across the interface into interstitial sites within the metal. This will result in a concentration gradient with con-

sequent diffusion of the H atoms into the interior of the metals via the interstitial sites of the lattice.

In the chemical desorption step the adsorbed H atoms diffuse about on the metal surface, either by threading their way through adsorbed water molecules or by pushing them aside, until two collide to form an H_2 molecule which escapes into the solution. This chemical step will be independent of overpotential, since charge transfer is not involved, and the rate will be proportional to the concentration or coverage θ_H of adsorbed H_{ads} . (see equation 20.39) and may occur at coverages that range from very small to almost complete.

On the other hand, the electrochemical desorption step is far more complex since it involves reaction between an adsorbed H atom, a hydrated proton H_3O^+ and an electron, and for desorption to occur the proton must discharge onto a hydrogen atom adsorbed on the metal surface. Under these circumstances the probability of collision will be low unless the coverage θ_H is high; furthermore, since coverage increases with overpotential, electrochemical desorption is more likely to occur at high negative overpotentials; in fact, in certain cases the mechanism will change from a C.D. to an E.D. step when the overpotential has attained a sufficiently large value.

Rate-determining Step

When a multistep reaction has attained a steady state the forward net rate $i_1 - i_1 = i_{c,1}$, etc.) of each step that constitutes the overall reaction must be equal. However, if one step requires a significantly higher energy of activation than any other that precedes or follows it, then the former will determine the overall rate, and is said to be the *rate-determining step* (r.d.s.).

This concept can be illustrated by considering two towns *A* and *C* separated by two interconnected roads *AB-BC*, of which *AB* is a motorway (maximum speed 70 m.p.h.) while *BC* is a narrow road and is controlled by regulations to a maximum speed of 30 m.p.h. (Fig. 20.19a). A driver going from *A* to *C* could proceed along *AB* at 70 m.p.h., but would then have to wait in a queue before entering *BC*, and owing to the congestion would not be able to exceed, say, 10 m.p.h. during his journey through it. To avoid queueing and the slow rate of transit through *BC* it would be necessary for all cars to proceed at, say, a constant speed of 25 m.p.h. for the whole journey, a rate that is determined by *BC* the rate-determining road (step). Figure 20.19b shows the standard free energy of activation against distance curves for a two-step reaction in which step 2 is rate determining. In the case of the h.e.r., either discharge (D.), chemical desorption (C.D.) or electrochemical desorption (E.D.) may be the r.d.s., and under these circumstances the other steps will be at equilibrium. Adopting the convention that \rightarrow represents the r.d.s. and that \rightleftharpoons represents the step at equilibrium, the possibilities are as follows:

D. followed by C.D.



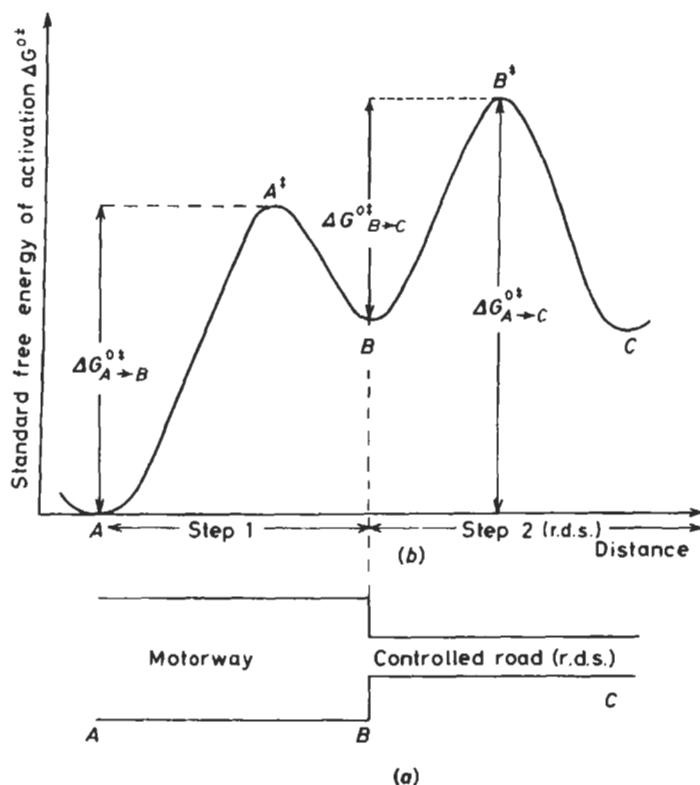
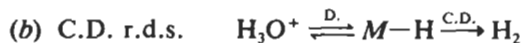
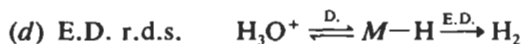
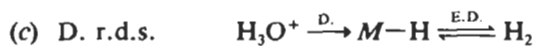


Fig. 20.19 (a) Analogy showing how the rate at which a car can travel from A to C is determined by the narrow controlled road BC (the r.d.s.). (b) Standard free energy of activation against distance for a two-step reaction; since the activation energy required to produce the activated state B^* is $\Delta G_{A \rightarrow C}^{\ddagger}$ and that to produce A is only $\Delta G_{A \rightarrow B}^{\ddagger}$, the former is the r.d.s., i.e. it is the height of the energy barrier compared with the initial state that determines the step that is rate determining



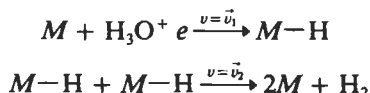
D. followed by E.D.



In the case of the step at equilibrium the rates of the forward and reverse reactions will be equal, i.e. $\vec{v}_1 = \overleftarrow{v}_1$, whereas in the case of the r.d.s. the rate of the reverse reaction $\overleftarrow{v}_{\text{r.d.s.}} = 0$, and $\vec{v}_{\text{r.d.s.}} = v_{\text{reaction}}$.

There are two further possibilities, which are referred to as coupled mechanisms, in which the rate of the reverse reaction of the first step is negligible and the forward reactions of both steps are coupled together. Thus both the reverse steps proceed at rates that are negligible, i.e. $\overleftarrow{v}_1 = \overleftarrow{v}_2 \rightarrow 0$.

It follows that for a coupled D. + C.D.



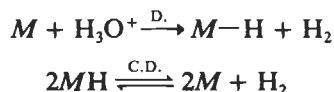
and a similar sequence of steps will occur for a coupled D. + E.D. mechanism.

Transfer Coefficient, Symmetry Factor and Stoichiometric Number

In Section 1.4 it was assumed that the rate equation for the h.e.r. involved a parameter, namely the transfer coefficient α , which was taken as approximately 0.5. However, in the previous consideration of the rate of a simple one-step electron-transfer process the concept of the symmetry factor β was introduced, and β was used in place of α , and it was assumed that the energy barrier was almost symmetrical and that $\beta \approx 0.5$. Since this may lead to some confusion, an attempt will be made to clarify the situation, although an adequate treatment of this complex aspect of electrode kinetics is clearly impossible in a book of this nature and the reader is recommended to study the comprehensive work by Bockris and Reddy¹.

In a multistep reaction the number of times the r.d.s. must occur for each act of the overall reaction is referred to as the *stoichiometric number* ν , and this concept can be illustrated by referring to the steps of the h.e.r.

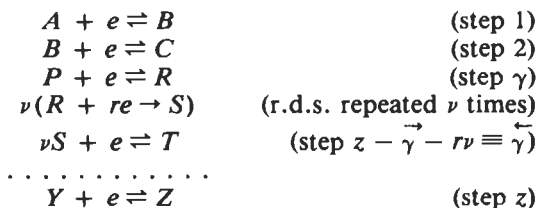
For rate-determining discharge followed by rapid C.D.



and since the discharge step must occur twice for each act of the overall reaction, $\nu = 2$. On the other hand, for rate-determining discharge followed by E.D.



the r.d.s. is required to take place only once, and $\nu = 1$. Generalising for a multistep reaction of the type $A + ze = Z$ in which all steps involve the transfer of one electron and the r.d.s. involves r electrons



where the convention adopted is that $\vec{\gamma}$ represents the number of steps that precede the r.d.s. and $\overleftarrow{\gamma}$ is the number that follow it. The r.d.s. will have to be repeated ν times if (a) more than R particles are formed by the preceding γ steps, or (b) more than one S particle is required for the following sequence involving $\overleftarrow{\gamma} = z - \vec{\gamma} - r\nu$ charge transfer steps, since ν electrons are transferred when the r.d.s. is repeated ν times. It can be shown that the total forward current is now

$$\vec{i} = i_0 \exp \left[- \left(\frac{\vec{\gamma}}{\nu} + r\beta \right) F\eta/RT \right] \quad \dots (20.86)$$

and that the total reverse current is

$$\overleftarrow{i} = i_0 \exp \left[\left(\frac{\overleftarrow{\gamma}}{\nu} + r - r\beta \right) F\eta/RT \right] \quad \dots (20.87)$$

Also, the net anodic current will be

$$i_a = \vec{i} - \overleftarrow{i}$$

and taking into account that $\overleftarrow{\gamma} \equiv z - \vec{\gamma} - r\nu$

$$i_a = i_0 \left\{ \exp \left[\left(\frac{z - \vec{\gamma}}{\nu} - r\beta \right) F\eta/RT \right] - \exp \left[- \left(\frac{\vec{\gamma}}{\nu} + r\beta \right) F\eta/RT \right] \right\} \quad \dots (20.88)$$

or

$$i_a = i_0 [e^{\vec{\alpha}F\eta/RT} - e^{-\overleftarrow{\alpha}F\eta/RT}] \quad \dots (20.89)$$

where the transfer coefficients $\overleftarrow{\alpha}$ and $\vec{\alpha}$ are defined by

$$\overleftarrow{\alpha} = \frac{z - \vec{\gamma}}{\nu} - r\beta \quad \dots (20.90)$$

and

$$\vec{\alpha} = \frac{\vec{\gamma}}{\nu} + r\beta \quad \dots (20.91)$$

These are the coefficients that determine the Tafel slope of the log i against η curve of a multistep reaction, and they are of fundamental importance in providing information on the mechanism of the reaction. Equations 20.86 and 20.87 are of the same form as equations 20.59 and 20.58 that were derived for a simple one-step reaction involving a symmetrical energy barrier, and under these circumstances equations 20.90 and 20.91 simplify to

$$\overleftarrow{\alpha} = 1 - \beta \approx 0.5 \quad \dots (20.92)$$

and

$$\vec{\alpha} = \beta \approx 0.5 \quad \dots (20.93)$$

and the transfer coefficients and symmetry factors are approximately the same. However, in multistep reactions equations 20.92 and 20.93 are not applicable, and the more complex transfer coefficients must be used in the rate equations.

Evaluation of the Rate-determining Step and the Mechanism of the h.e.r.

The slope of the Tafel curve $d\eta/d \log i$ is only one of the criteria that are required to determine the mechanism of the h.e.r., since different mechanisms, involving different r.d.s. often have the same Tafel slope. Parameters that are diagnostic of mechanism are the transfer coefficient, the reaction order, the stoichiometric number, the hydrogen coverage, the exchange current density, the heat adsorption, etc.

The ability to use the Tafel slope as a diagnostic criterion can be exemplified by considering a discharge-chemical desorption mechanism for the h.e.r. in which either discharge or chemical desorption may be rate determining².

If the discharge step is rate determining, then for step 1

$$i = i_0 \exp(-\beta F \eta / RT) \quad \dots (20.94)$$

and by taking logarithms of both sides and rearranging

$$\eta = \frac{RT}{\beta F} \ln i_0 - \frac{RT}{\beta F} \ln i = 2.3 \frac{RT}{\beta F} \log i_0 - 2.3 \frac{RT}{\beta F} \log i \quad \dots (20.95)$$

and differentiating

$$\frac{d\eta}{d \log i} = -2.3 \frac{RT}{\beta F} = -2.3 \frac{RT}{0.5F} \quad \dots (20.96)$$

if β is taken to be 0.5.

$$\therefore \frac{d\eta}{d \log i} = -2 \times 0.059 = -0.118 \text{ V at } 298 \text{ K} \quad \dots (20.97)$$

Thus a Tafel slope of -0.118 V/decade could be diagnostic of a discharge-chemical desorption mechanism in which proton discharge is the r.d.s.

If chemical desorption is rate determining, the rate will be independent of overpotential since no charge transfer occurs in this step, and

$$v_{C.D} = k_{C.D.} c_{H_{ads}} \times c_{H_{ads}} = k \theta_H^2 \quad \dots (20.98)$$

The discharge step will now be at equilibrium and can be treated thermodynamically

$$\begin{aligned} H^+ + e &\rightleftharpoons H_{ads.} \\ E &= E^\circ + \frac{RT}{F} \ln \frac{c_{H^+}}{c_{H_{ads.}}} = E^\circ + \frac{RT}{F} \ln \frac{c_{H^+}}{\theta_{H_{ads.}}} \quad \dots (20.99) \end{aligned}$$

where c_{H^+} is the concentration of H_3O^+ in solution.

$$\therefore \theta_H = c_{H^+} \exp[-F(E - E^\circ)/RT] \quad \dots (20.100)$$

Now $\eta = E - E_{eq.}$, and since E° is a constant and $E_{eq.}$ will be constant if c_{H^+} is constant, we can replace $E - E^\circ$ with η and

$$\theta_H = k_D \exp(-F\eta/RT) \quad \dots (20.101)$$

where k_D is the rate constant for the discharge step.

Now although the chemical desorption step is independent of η , the surface coverage will increase as η becomes more negative and this will affect $v_{C.D.}$. Since two electrons will be required for the overall reaction, equation 20.98 can be expressed in terms of i

$$v_{C.D.} = \frac{i}{2F} = k_{C.D.} \theta_H^2 \quad \dots (20.102)$$

Combining equations 20.101 and 20.102

$$i = 2Fk_{C.D.} [k_D \exp(-F\eta/RT)]^2 \quad \dots (20.103)$$

or

$$i = K \exp(-2F\eta/RT) \quad \dots (20.104)$$

and taking logarithms and rearranging

$$\eta = \frac{RT}{2F} \ln K - \frac{RT}{2F} \ln i \quad \dots (20.105)$$

where K is a constant that contains all the other constants (F , k_D , $k_{C.D.}$). Differentiating

$$\frac{d\eta}{d \log i} = \frac{-2.3 RT}{2F} = \frac{-0.059}{2} = -0.030 \text{ V} \quad \dots (20.106)$$

which is the Tafel slope obtained with platinum for which the h.e.r. in acid solution follows a discharge-chemical desorption mechanism in which chemical desorption is rate determining and $\theta \rightarrow 1$.

Table 20.3 summarises the possible mechanism for the h.e.r. at various metals¹⁹.

Table 20.3 Mechanism of the hydrogen evolution reaction at different metals (data after McBreen and Genshaw¹⁹)

							Al D			
Ti D			Mn A	Fe E, C	Ni A	Cu A or D		Ga A		
	Nb D	Mo D			Rh B	Pd B	Ag C or D	Cd A	Sn A	
	Ta D	W A or D			Ir B	Pt B	Au D	Hg A	Tl A	Pb A
										Bi D

A Slow discharge, fast recombination.

B Fast discharge, slow recombination.

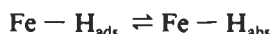
C Slow discharge, fast electrochemical.

D Fast discharge, slow electrochemical.

E Coupled discharge recombination.

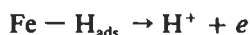
Hydrogen Evolution on Iron

A number of metals have the ability to absorb hydrogen, which may be taken into solid solution or form a metallic hydride, and this absorption can provide an alternative reaction path to the desorption of $H_{ads.}$ as H_2 gas. In the case of iron and iron alloys, both hydrogen adsorption and absorption occur simultaneously, and the latter thus gives rise to another equilibrium involving the transfer of $H_{ads.}$ across the interface to form interstitial H atoms just beneath the surface:



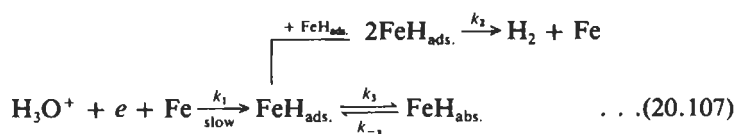
This equilibrium is of importance in providing diagnostic criteria for the mechanism of the h.e.r., since the rate of permeation of hydrogen through a thin iron membrane can provide information on the coverage of the surface with adsorbed hydrogen.

Devanathan and Stachurski¹⁷ have devised a two-compartment cell which has been widely used for studying the permeation of hydrogen through iron and ferrous alloys and other metals. The cell consists of two compartments separated by a thin diaphragm of the metal under study; the cathode compartment, which contains an appropriate electrolyte solution and a counter-electrode, is used to polarise cathodically one side of the membrane at a constant current density or potential. A feature of the cell is the electrochemical estimation of the hydrogen that permeates through the diaphragm, which is achieved by maintaining the reverse side of the diaphragm (the anode side) at a constant potential in 0.1 M NaOH and oxidising the adsorbed hydrogen by the reaction



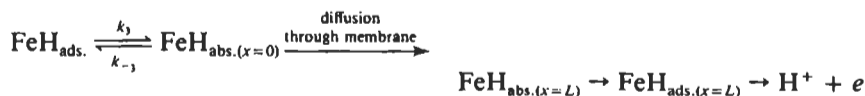
The anode compartment contains a reference electrode and counterelectrode and by means of a potentiostat the anode side is maintained at a constant potential. The coverage of adsorbed hydrogen θ_H on the cathode side will depend on the current density i and the nature of the electrolyte solution, and the cell can be used to study the effect of a variety of factors (composition and structure of alloys, pH of solution, effect of promoters and inhibitors) on hydrogen permeation.

Bockris, McBreen and Nanis¹⁸ have studied the h.e.r. on pure iron in 0.1 M NaOH and 0.1 M H_2SO_4 , and have concluded that in both cases the reaction mechanism is coupled discharge-chemical desorption at low coverages (Langmuirean adsorption) with the discharge step being rate determining; in NaOH at very negative overpotentials (> -1.02 V) there appears to be a change in the mechanism to slow discharge-fast electrochemical desorption at high coverages. The reaction sequence can be summarised as follows



where k_1 , k_2 , k_3 and k_{-3} are the rate constants for the different steps.

The permeation of hydrogen through an iron diaphragm is illustrated in Fig. 20.20 for the sequence of events



where $\text{FeH}_{\text{abs.}(x=0)}$ refers to the hydrogen absorbed just below the surface of the cathode side of the membrane and $\text{FeH}_{\text{abs.}(x=L)}$ that just below the absorbed surface on the anode side.

At the steady state the flux of hydrogen J_∞ will be

$$J_\infty = \frac{Dc_0}{L} \quad \dots (20.108)$$

where D is the diffusion coefficient, L is the thickness of the membrane and c_0 is the concentration of H at $x = 0$; the concentration of hydrogen just below the surface on the anode side c_L will be zero owing to the rapid removal of the $\text{H}_{\text{ads.}}$ by electrochemical oxidation (Fig. 20.20). Since diffusion through the membrane will be slow compared to the other steps it will be rate determining, and the rate of transfer of $\text{H}_{\text{ads.}}$ from the surface to the bulk and of $\text{H}_{\text{abs.}}$ from the bulk to the surface will be at equilibrium (equation 20.107).

$$\therefore k_3\theta = \left(1 - \frac{x_0}{x_s}\right) = k_{-3}c_0(1 - \theta) \quad \dots (20.109)$$

where x_0 is the number of interstitial sites per cubic centimetre beneath the surface that are occupied by hydrogen, x_s is the total number of sites available and c_0 is the concentration of hydrogen at $x = 0$.

At low coverages and low concentrations, equation 20.109 simplifies to

$$k_3\theta = k_{-3}c_0, \text{ or } c_0 = \frac{k_3\theta}{k_{-3}} \quad \dots (20.110)$$

which shows that c_0 is proportional to the coverage of the cathode side with $\text{H}_{\text{ads.}}$. From equations 20.108 and 20.110 the flux through the diaphragm will be

$$J_\infty = \frac{D}{L} \left(\frac{k_3}{k_{-3}} \right) \theta \quad \dots (20.111)$$

and if J_∞ is the permeation current ($\mu\text{A cm}^{-2}$) at the steady state, then

$$\frac{J_\infty}{zF} = \frac{D}{L} \left(\frac{k_3}{k_{-3}} \right) \theta$$

or

$$J_\infty = \frac{DzF}{L} \left(\frac{k_3}{k_{-3}} \right) \theta \quad \dots (20.112)$$

which shows that the permeation current is proportional to coverage with $\text{H}_{\text{ads.}}$.

For the reaction sequence shown in equation 20.107 the cathodic current

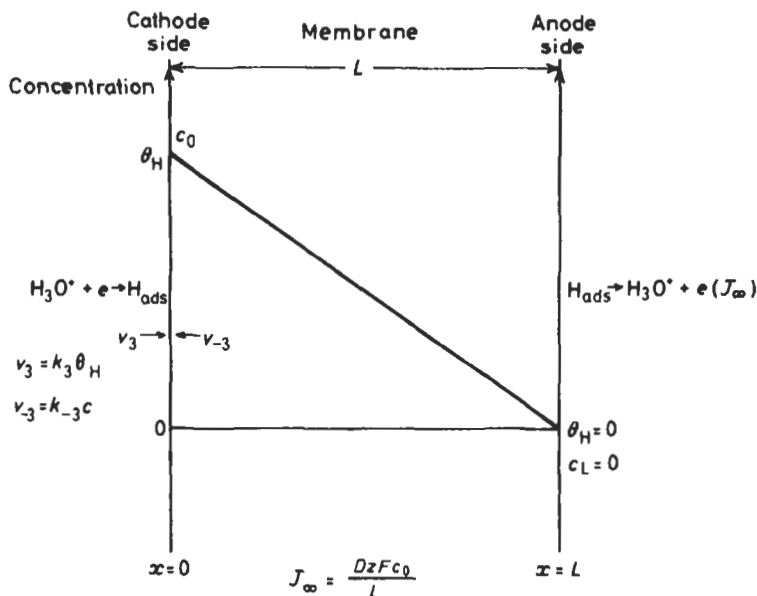


Fig. 20.20 Permeation of hydrogen through a thin iron membrane

is given by

$$\vec{i} = k_1 c_{H^+} (1 - \theta) e^{-\beta \eta F / RT} = k_2 \theta^2 \quad \dots (20.113)$$

since the rate of discharge and chemical desorption must be equal.

$$\therefore \theta = \left(\frac{1}{k_2} \right)^{\frac{1}{2}} i^{\frac{1}{2}} \quad \dots (20.114)$$

and from equation 20.112

$$J_\infty = \frac{DzF}{L} \left(\frac{k_3}{k_{-3}} \right) \left(\frac{1}{k_2} \right)^{\frac{1}{2}} i^{\frac{1}{2}} \quad \dots (20.115)$$

which shows that J_∞ is linearly related to $i^{\frac{1}{2}}$, i.e.

$$J_\infty \propto i^{\frac{1}{2}} \quad \dots (20.116)$$

Also for the reaction sequence shown in equation 20.107

$$J_\infty = \frac{DzF}{L} c_{H^+}^{\frac{1}{2}} \left(\frac{k_3}{k_{-3}} \right) \left(\frac{k_1}{k_2} \right) e^{-\beta \eta F / 2RT}$$

where η is the overpotential, and taking $\beta \approx 0.5$ and differentiating

$$\frac{\partial \eta}{\partial \ln J_\infty} \approx -\frac{4RT}{F} \quad \dots (20.117)$$

or

$$\frac{\partial \eta}{\log J_\infty} \approx -0.059 \times 4 = -0.24 \text{ V at } 25^\circ \text{C} \quad \dots (20.118)$$

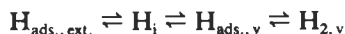
From the magnitude of the Tafel slope $\partial\eta/\partial \log i$ (≈ 0.12 V), the magnitude of $\partial\eta/\partial \ln J_\infty$ (≈ 0.24 V) and the linearity of the J vs. $i^{1/2}$ curves for pure iron in H_2SO_4 and NaOH at various temperatures in the range 18–80°C, Bockris, *et al.*¹⁸ concluded that the mechanism conformed to the reaction sequence shown in equation 20.107.

Diagnostic criteria ($\partial\eta/\partial \log i$ and $\partial\eta/\partial \log J$ slopes, and J against $f(i)$ relationships) for the various mechanisms of the h.e.r. for Langmuir and Temkin adsorption have been derived and tabulated by McBreen and Genshaw¹⁹.

Electrochemical Aspects of Hydrogen Embrittlement

Mild-steel tanks used for containing acid solutions sometimes develop large blisters on their outer surface, which are due to hydrogen within the steel exerting a pressure sufficiently high to cause plastic deformation of the steel. The atomic hydrogen formed by reaction of the steel with the acid diffuses through the steel and segregates at voids or traps in the metal where it combines to form high-pressure molecular hydrogen. Although blister formation is seldom observed with high-tensile steels it is not unreasonable to assume that hydrogen at high pressures is largely responsible for their embrittlement and for the phenomenon of delayed failure. Theories of hydrogen embrittlement are considered in Section 8.4, but it is appropriate here to review briefly the electrochemical aspects of hydrogen discharge and absorption with particular reference to the pressure developed by hydrogen occluded at traps and voids.

The permeation cell devised by Devanathan and Stachurski¹⁷ has provided a most valuable tool for studying the effect of alloy composition and structure²⁰, tensile^{21,22} and compressive stresses²³, partial pressure of hydrogen^{22,24}, etc. on the permeation of hydrogen through ferrous alloys, and the results obtained have lead to a greater insight into the mechanism of embrittlement. In the above discussion on hydrogen permeation through iron it was assumed that diffusion occurred via the interstitial sites of a perfect lattice of the metals. However, in real metals and alloys imperfections exist in the lattice that are referred to as traps or voids, and which may consist of imperfections in the lattice, interfacial areas between phase boundaries, inclusions, etc. (see Section 8.4). Hydrogen diffusing interstitially through the lattice can adsorb at the surface of these trapping sites and then combine to form molecular hydrogen at a pressure that will depend on the overpotential at the charged surface. If an iron electrode is cathodically charged with hydrogen there will be an equilibrium between the hydrogen adsorbed at the external surface $\text{H}_{\text{ads., ext.}}$, hydrogen at interstitial sites H_i , hydrogen adsorbed at the surface of voids $\text{H}_{\text{ads., v}}$ and molecular hydrogen within the void $\text{H}_{2, \text{v}}$.



and thermodynamically

$$\mu_{\text{H}_{\text{ads., ext.}}} = \mu_{\text{H}_i} = \mu_{\text{H}_{\text{ads., v}}} = \mu_{\text{H}_{2, \text{v}}}$$

where μ is the chemical potential. Thus the chemical potential of the hydrogen adsorbed on the external surface will equal the chemical potential (fugacity) of the molecular hydrogen within the void.

It can be shown²⁵ that

$$\frac{\theta}{1-\theta} = \frac{\theta_{rev}}{1-\theta_{rev}} \times p_{H_2,v}^{\frac{1}{2}} \quad \dots (20.119)$$

where θ is the surface coverage, θ_{rev} the reversible coverage at 1 atm of H_2 (approx. 10^{-3} for pure iron in a solution of pH = 4) and p_{H_2} is the fugacity of H_2 within the traps. The pressure of hydrogen will increase, therefore, with surface coverage of $H_{ads, ext.}$, and this in turn will be dependent on the overpotential and the mechanism of the h.e.r. It was considered at one time that the fugacity of hydrogen could be evaluated from the Nernst equation, but Bockris and Subramanyan²⁵ on the basis of statistical mechanics have derived the η vs. p_{H_2} relationship for the possible mechanisms of the h.e.r. and have shown that the Nernst equation is not always applicable. Thus for a fast discharge-slow desorption mechanism (either chemical or electrochemical) in which $\theta \rightarrow 1$, the relationship between the fugacity of H_2 in voids $p_{H_2,v}$ at an external pressure of hydrogen of 1 atm is given by

$$p_{H_2,v} = \exp \left(\frac{-2\eta F}{RT} \right) \quad \dots (20.120)$$

which is identical to the relationship derived from the Nernst equation. On the other hand, for a coupled discharge-chemical desorption mechanism (applicable to pure iron) the fugacity is given by

$$p_{H_2,v} = 10^{1.5} \exp \left(\frac{-\eta F}{2RT} \right) \quad \dots (20.121)$$

If the overpotential is taken as -0.1 V it follows from equation 20.120 that $p_{H_2,v} = 10^{3.3}$ atm. Although the arguments used in deriving these relationships do not give precise values of $p_{H_2,v}$ they indicate that pressures of very high magnitude will be obtained at significant overpotentials.

The effect of stress²¹ on hydrogen solubility and permeation is clearly of vital importance in relation to delayed failure, since fracture can only occur if the metal is subjected to a tensile stress (internal or applied). It has been reported that high-strength steels containing <0.1 p.p.m. of hydrogen are susceptible to fracture at applied stresses well below the yield stress, and Troiano²⁶ has postulated that diffusion of hydrogen to regions of high triaxial stress is of major importance in the mechanism of embrittlement.

Beck, *et al.*²¹ have used the permeation technique to study the effect of uniaxial tensile stresses in the elastic region on hydrogen permeation through pure iron, and have shown that it increases with increase in stress. The partial molar volume of hydrogen \bar{V}_H (cubic centimetres of hydrogen per mole of iron) in ferrous alloys can be evaluated from the variation of permeation with applied stress, and from the relationship

$$c_\sigma = c_0 e^{\sigma \bar{V}_H / RT} \quad \dots (20.122)$$

where σ is the applied stress, and c_0 and c_σ are the hydrogen solubilities in the absence of a stress, and in its presence, respectively. The concentration

terms can be replaced by the corresponding permeation terms J_0 and J_σ and equation 20.122 then becomes

$$J_\sigma = J_0 e^{\sigma \bar{V}_H / RT} \quad \dots (20.123)$$

or

$$\frac{\partial \ln(J_\sigma / J_0)}{\partial \sigma} = \frac{\bar{V}_H}{RT} \quad \dots (20.124)$$

Thus a plot of $\log(J_\sigma / J_0)$ against σ gives a straight line of slope $\bar{V}_H / 2.3 RT$, which provides a means of evaluating \bar{V}_H ; for pure iron the partial molar volume has been found to be $2.6 \text{ cm}^3 \text{ mol}^{-1}$, but the value has been found to vary with the composition and structure of the steel²². It follows from equation 20.122 that when σ is tensile (taken as positive in equation 20.122) the solubility of hydrogen and the permeation rate will increase, i.e. the larger the lattice distortion the greater the solubility; conversely, compressive stresses (σ is negative) will decrease solubility, as may be shown by permeation studies of steels under compression, or by putting the surface of the metal into a state of compressive stress by shot peening²³.

Bockris and Subramanyan²⁷ during studies of the permeation of hydrogen through pure Fe and Fe-5Ni alloy found that a normal permeation transient was obtained (Fig. 20.21), providing the overpotential was less than a critical value, and when the overpotential was less than $\eta_{\text{crit.}}$ it was possible to reproduce the normal permeation curve, i.e. apply the polarising current at a constant $\eta < \eta_{\text{crit.}}$ allow J to attain a steady value, switch off, reapply

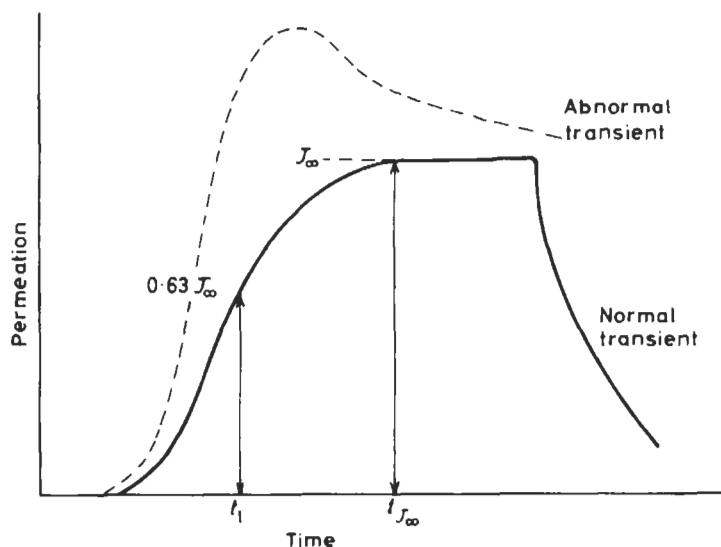


Fig. 20.21 J - t transients for the permeation of hydrogen through ferrous alloys. The normal transient enables the diffusion coefficient D to be evaluated from the relationship $t_1 = L^2/6D$, where t_1 is the time at which J attains a value of 0.63 of the steady-state permeation J

polarising current, etc. However, if $\eta_{\text{crit.}}$ was exceeded, a second determination of the J - t transient resulted in an abnormal curve that showed a more rapid rise time than the normal curve, and a peak (Fig. 20.21); furthermore, after the determination of the transient at or above $\eta_{\text{crit.}}$ it was not possible to obtain a normal transient at an overpotential less than $\eta_{\text{crit.}}$ Anomalous decay transients were also obtained.

On the basis of the Griffith crack theory, and by assuming that the void has the shape of a double convex lens with a long axis of length l , Bockris and Subramanyan²⁷ derived an expression for the critical stress, corresponding with the critical pressure of hydrogen within the void required to cause the void to grow and for a crack to be initiated:

$$\sigma_{\text{crit.}} = p_{\text{H}_2, \text{v}} > \left[\frac{16}{3} \times \frac{Y\gamma}{l} \right]^{\frac{1}{2}} \quad \dots (20.125)$$

where Y is Young's modulus and γ is the surface tension of the M - H interface at the surface of the void ($S\gamma$ is the total surface energy, where S is the surface area of the void). Taking typical values of Y , σ and l it can be calculated that $p_{\text{H}_2} \approx 3 \times 10^4$ atm, which is a pressure that could be achieved at overpotential greater than a critical value. An extensive review of hydrogen in metals is given in a publication by Subramanyan²⁸.

L. L. SHREIR

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20.2 Outline of Chemical Thermodynamics

Scope

Thermodynamics is concerned with the relationship between heat energy and work and is based on two general laws, the 1st and 2nd laws of thermodynamics, which both deal with the interconversion of the different forms of energy. The 3rd law states that at the absolute zero of temperature the entropy of a perfect crystal is zero, and thus provides a method of determining absolute entropies.

The following features of the thermodynamic approach to chemical reactions should be noted:

1. It does not involve time as a variable, and does not provide information on rates.
2. It does not normally involve a knowledge of the detailed structure of the system nor of the detailed mechanism of the reaction.
3. The 2nd law is true only statistically and does not apply to individual particles nor to a small number of particles, i.e. thermodynamics is concerned with bulk properties of systems. Thermodynamics thus has many limitations, but is particularly valuable in defining the nature and structure of phases when *equilibrium* (a state that does not vary with time) has been attained; thermodynamics provides no information on the *rate* at which the reaction proceeds to equilibrium, which belongs to the realm of *chemical kinetics*.

Some Definitions

A *system* is any part of external reality that can be subjected to thermodynamic treatment; the material with which the system is in contact forms the *surroundings*, e.g. an electrochemical cell could be the system and the external atmosphere the surroundings.

A *homogeneous* system is one in which the properties are uniform or vary uniformly throughout the system, whereas a *heterogeneous* system is one consisting of two or more homogeneous systems. Pure copper and a pure solution of CuSO_4 are both homogeneous systems, but copper immersed in a solution of CuSO_4 is a heterogeneous system characterised by an interface. The state of a system is described by its properties, which may be *intensive* or *extensive*; intensive properties are independent of quantity, e.g.

temperature, pressure, electrical potential, activation energy, etc. whereas extensive properties depend upon the amount of the material, e.g. mass, volume, internal energy, enthalpy, entropy, free energy, chemical potential, etc.

The state of a system containing a constant amount of material depends upon a few variables, e.g. pressure p , volume V , temperature T . For a given mass of pure substance the volume can be expressed solely as a function of pressure and temperature

$$V = f(p, T) \quad \dots (20.126)$$

If the pressure changes from p to $p + dp$ and the temperature from T to $T + dT$ the change in V is given by

$$dV = \left(\frac{\partial V}{\partial p} \right)_T dp + \left(\frac{\partial V}{\partial T} \right)_p dT \quad \dots (20.127)$$

where $\left(\frac{\partial V}{\partial p} \right)_T$ is the rate of change of volume with pressure at constant temperature, and $\left(\frac{\partial V}{\partial T} \right)_p$ is the rate of change of volume with temperature at constant pressure. They are referred to as *partial derivatives*, the subscript T or p denoting the variable that is maintained constant.

A *reversible* system is one which is so perfectly balanced that only an infinitesimal change in external conditions is required to reverse the direction of the process; for reversibility the change must either be infinitesimally small or if large it must be carried out at an infinitely slow rate. Although these concepts are hypothetical it is possible to approximate to reversibility by balancing the e.m.f. of a reversible cell with the e.m.f. of a potentiometer circuit so that only a minute change ($< 10^{-6}$ V) in the e.m.f. produced by the latter will result in a reversal of the direction of the cell reaction. An ideal reversible cell must consist of two reversible electrodes, which are so completely non-polarisable that their potentials are unaffected by charge transfer even at high rates. This too is a hypothetical concept, but a number of electrodes will approximate to reversibility, providing the rate of charge transfer is small, and cells composed of these electrodes may be treated thermodynamically. (See Chapter 20.3.)

1st Law of Thermodynamics

The 1st law is essentially a statement of the experimental fact that during a chemical reaction in an isolated system *energy is conserved*, although it may be converted from one form to another.

If a system changes from state A to state B and if ΔU is the change in the internal energy of the system, then it follows from the 1st law that the surroundings must gain or lose an equivalent amount of energy. A convention of signs is necessary to take into account the direction of heat transfer q and work performed w ; q is taken as positive if heat is transferred to the system from the surroundings and negative if the transfer is in the reverse direction; in many textbooks w is taken as positive if work is done by the system on the surroundings and negative if work is done to the system by

the surroundings, but it is preferable to allow the sign of w to develop from the mathematics. Thus, since energy must be conserved

$$\Delta U = q - w \quad \dots (20.128)$$

where ΔU is the change in the internal energy of the system, q is the heat transferred between the system and the surroundings and w is the work done. Equation 20.128 may be regarded as an algebraic expression of the conservation of energy, and it should be noted that ΔU is the difference in the internal energy of the system in its initial and final stages and that the absolute value of U is not known.

If a change from state A to state B occurs in a system at constant pressure (isobaric) so that only pV work is done, then $w = p\Delta V$ and

$$\Delta U = q_p - p(V_B - V_A) \quad \dots (20.129)$$

which can be written in the form

$$q_p = U_B - U_A + p(V_B - V_A) = (U_B + pV_B) - (U_A + pV_A) \quad \dots (20.130)$$

Thus it is convenient to define another function

$$H = U + pV \quad \dots (20.131)$$

where H is the *enthalpy* or *heat content* of the system, so that

$$q_p = H_B - H_A = \Delta H \quad \dots (20.132)$$

where q_p is the heat exchanged between the system and the surroundings at constant pressure, and ΔH , like ΔU , depends only upon the initial and final states of the system.

2nd Law of Thermodynamics

The 1st law implies that energy is interconvertible and that when one form of energy disappears another kind of energy must appear in its place. However, it provides no information on (a) the transformations of energy that are possible, and (b) the extent to which one form of energy can be converted into another. Some energy transformations are possible and occur spontaneously, whilst transformations in the reverse direction are non-spontaneous and can be made to proceed only by supplying energy from an external source. Thus heat will flow spontaneously from a source at a higher temperature to one at a lower temperature, but heat cannot pass spontaneously in the reverse direction. The heat flowing spontaneously can be converted by means of suitable machinery to work energy, but it is evident from Carnot's cycle (p. 20:60) that there is a theoretical limit to the extent of this interconversion.

The oxidation of hydrogen to water ($H_2 + \frac{1}{2}O_2 \rightarrow H_2O$) is thermodynamically spontaneous and the energy released as a result of the chemical reaction appears as heat energy, but the decomposition of water into its elements is a non-spontaneous process and can be achieved only by supplying energy from an external source, e.g. a source of e.m.f. that decomposes the water electrolytically. Furthermore, although the heat produced by the spontaneous reaction could be converted into electrical energy, the electrical

energy thus obtained would not be sufficient to restore the original state of chemical energy of the system, i.e. to regenerate 1 mol H_2 and $\frac{1}{2}$ mol O_2 .

The 2nd law, which can be stated in a number of different ways, expresses the fact that heat can only be transformed into work when it flows from a higher to a lower temperature. Clausius, stated the 2nd law as follows: 'It is impossible for a self-acting machine, unaided by an external agency, to convey heat from a lower to a higher temperature'.

In principle all spontaneous processes may be harnessed and made to do work, but owing to the wastage of a proportion of the energy as heat energy there is a theoretical limit to the amount of useful work that can be obtained, and this can never be exceeded in practice. A high-efficiency power station converting chemical energy (solid or liquid fuel) into electrical energy achieves only 30–40% efficiency.

The maximum theoretical work $w_{\text{max.}}$ obtainable from a system was derived by Carnot who considered the transformation of heat energy into work when a perfect gas in a cylinder with a piston was taken through a reversible cycle (the Carnot cycle), in which the system was almost at equilibrium during each step of the cycle. It was shown that

$$w_{\text{max.}} = q_2 \left(\frac{T_2 - T_1}{T_2} \right) \quad \dots (20.133)$$

where q_2 is the heat absorbed from a reservoir at the higher temperature T_2 (K) and T_1 is the temperature of a second heat reservoir at a lower temperature than T_2 that receives the heat that has not been converted into work. Equation 20.133 is applicable to any reversible system that undergoes a cyclic process in which the original and final states of the system and the surroundings are the same. Under these circumstances all that has changed permanently is that a quantity of heat q_2 at T_2 has been transformed into work $w_{\text{max.}}$ together with a quantity of heat $q_1 = q_2 - w_{\text{max.}}$ that is returned to the reservoir at the lower temperature T_1 . It can be shown that the efficiencies of all reversible cyclic processes are the same providing T_1 and T_2 are the same, i.e.

$$\text{Thermodynamic efficiency} = \frac{w_{\text{max.}}}{q_2} = \frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2} \quad \dots (20.134)$$

It is evident from equation 20.134 that (a) the efficiency increases as $(T_2 - T_1)/T_2$ increases and (b) the efficiency is zero when $T_1 = T_2$ so that no heat can be converted into work.

Entropy

The concept of entropy S is implicit in the 2nd law, and it may be regarded as a thermodynamic property of a system that is associated with its capacity for spontaneous change. As the system undergoes spontaneous change the entropy increases and the capacity for further spontaneous change decreases. Rearranging the q and T terms in equation 20.134 and applying the convention of signs

$$\frac{q_1}{T_1} - \frac{q_2}{T_2} = 0 \quad \dots (20.135)$$

and generalising for any reversible cyclic change that proceeds isothermally at a temperature T

$$\sum \frac{q_{\text{rev.}}}{T} = 0 \quad \dots (20.136)$$

where $\sum q_{\text{rev.}}$ is the sum of the heats absorbed or evolved reversibly. The function $q_{\text{rev.}}/T$ is a measure of the change in entropy ΔS , and this change for an isothermal process is defined as

$$\Delta S = \frac{q_{\text{rev.}}}{T} \quad \dots (20.137)$$

and for an infinitesimal reversible process

$$dS = \frac{\delta q}{T} \quad \dots (20.138)$$

If the process is non-isothermal but finite

$$\Delta S = S_2 - S_1 = \int_{S_1}^{S_2} \frac{\delta q}{T} \quad \dots (20.139)$$

It must be emphasised that the heat $q_{\text{rev.}}$ which appears in the definition of entropy (equation 20.137) is always that absorbed (or evolved) when the process is conducted reversibly. If the process is conducted irreversibly and the heat absorbed is q , then q will be less than $q_{\text{rev.}}$ and q/T will be less than ΔS the entropy change (equation 20.137). It follows that if an irreversible process takes place between the temperatures T_2 and T_1 and has the same heat intake q at the higher temperature T_2 as the corresponding reversible process, the efficiency of the former must be less than that of the latter, i.e.

$$\left(\frac{q_1}{T_1} - \frac{q_2}{T_2} \right)_{\text{irrev.}} > \left(\frac{q_1}{T_1} - \frac{q_2}{T_2} \right)_{\text{rev.}} \quad \dots (20.140)$$

Thus from equations 20.136 and 20.140 it follows that for an irreversible cycle

$$\sum \frac{q}{T} > 0 \quad \dots (20.140a)$$

and that the more positive $\sum q/T$ is the more irreversible is the cycle. In the Carnot cycle each stage is carried out reversibly and the entropy change is zero, and it can be shown that any complete cycle can be reduced to the sum of a large number of infinitesimal Carnot cycles so that the entropy change for any complete reversible cycle must always be zero. Thus for any reversible process the sum of all entropy changes for all systems participating is given by

$$\sum dS = 0 \quad \dots (20.141)$$

which provides a criterion for equilibrium.

On the other hand, in any irreversible process although the system may gain (or lose) entropy and the surroundings lose (or gain) entropy, the system plus surrounding will always gain in entropy (equation 20.141). Thus for a real process proceeding spontaneously at a finite rate

$$\Sigma dS > 0 \quad \dots (20.142)$$

For example, if a hot body (the system) is in contact with the surroundings at an infinitesimally lower temperature there will be an isothermal and reversible transfer of heat at T_2 , and the loss in entropy of the hot body will be $\Delta S_b = -q_{rev}/T_2$ and the gain in entropy of the surroundings will be $\Delta S_s = +q_{rev}/T_2$, and $\Delta S_b + \Delta S_s = 0$. On the other hand, if the surroundings are at a lower temperature T_1 than the body the transfer of heat will be irreversible and spontaneous, and the entropy changes will be $\Delta S_b = -q_{rev}/T_2$ and $\Delta S = +q_{rev}/T_1$. Since $T_2 > T_1$ the total change in entropy will be greater than zero, and the greater the difference between T_2 and T_1 the greater the gain in the total entropy of the system as a whole, i.e. the more spontaneous or irreversible is the transfer of heat.

When a substance is heated at constant pressure without change of phase through a temperature rise dT the heat absorbed is $C_p dT$, where C_p is the molar heat capacity at constant pressure, and the entropy increase is

$$\int_{S_1}^{S_2} dS = \int_{T_1}^{T_2} \frac{C_p}{T} dT = \int_{T_1}^{T_2} C_p d \ln T \quad \dots (20.143)$$

Thus the entropy increase when the substance is heated from T_1 to T_2 is

$$\Delta S = \int_{T_1}^{T_2} C_p d \ln T = 2.303 \int_{T_1}^{T_2} C_p d \log T \quad \dots (20.144)$$

and ΔS may be evaluated by determining the heat capacity C_p at various temperatures between T_2 and T_1 , and plotting the values against $\log T$; the area enclosed by the curve multiplied by 2.303 gives the entropy increase. When there is a change of phase such as the evaporation of a liquid to saturated vapour, melting of a solid to a liquid or transition from one crystalline form to another, the process is isothermal and reversible, and

$$\Delta S = \frac{q}{T} \quad \dots (20.145)$$

where q is the heat associated with the phase change at T .

For example, in the case of the reversible isothermal transformation of ice to water at the melting point (273 K), the heat gained by the ice will be the latent heat of fusion ($\Delta H_f = 6006 \text{ J mol}^{-1}$) and a corresponding quantity of heat will be lost by the surrounding, and

$$\Delta S_{\text{system}} = \Delta S_{\text{ice}} + \Delta S_{\text{surr.}} = \frac{6006}{273} - \frac{6006}{273} = 0$$

Gibbs Free Energy or Free Enthalpy

The Gibbs free energy G provides a means of defining equilibrium or of the tendency of a reaction to proceed in a given direction. It is similar to the

other thermodynamic functions described above in that the change in free energy ΔG is determined solely by the initial and final states of the system. The maximum work, or maximum available energy, defined in terms of the Gibbs free energy G , which is now called the *free enthalpy*, is

$$G = H - TS \quad \dots (20.146)$$

or, for a finite change

$$\Delta G = \Delta H - T\Delta S \quad \dots (20.147)$$

It can be shown that for a system in which the total mass, or the concentrations of the components, remains constant

$$\left(\frac{\partial G}{\partial P}\right)_{T, n_i, \dots} = V \quad \dots (20.148)$$

and

$$\left(\frac{\partial G}{\partial T}\right)_{P, n_i, \dots} = -S \quad \dots (20.149)$$

Combining equations 20.146 and 20.149

$$G - H = T \left(\frac{\partial G}{\partial T}\right)_{P, n_i, \dots} \quad \dots (20.150)$$

which is the important Gibbs-Helmholz equation. Since in thermodynamics we are concerned mainly with changes in free energy and enthalpy, equation 20.150 can be written

$$\Delta G - \Delta H = T \left(\frac{\partial \Delta G}{\partial T}\right)_{P, n_i, \dots} \quad \dots (20.151)$$

Units Free energy is an *extensive* quantity, but the *standard* free energy for 1 mol $\Delta G_{298\text{ K}}^\circ$ (in units of J mol^{-1}) defined above is an *intensive* quantity.

The Chemical Potential

The energy of a system can be changed by means of thermal energy or work energy, but a further possibility is to add or subtract moles of various substances to or from the system. The free energy of a pure substance depends upon its chemical nature, its quantity (ΔG is an extensive property), its state (solid, liquid or gas), and temperature and pressure. Gibbs called the partial molar free heat content (free energy) of the i^{th} component of a system its *chemical potential*

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j} \quad \dots (20.152)$$

i.e. the change in free enthalpy of the system when 1 mol of component i is added to the system, the T , P and concentration of all other substances (n_j) being maintained constant. The partial molar free energy of a pure compound is synonymous with the *standard chemical potential* μ° , which is the free enthalpy change when 1 mol of the substance is formed from its

elements under isothermal isobaric conditions. In order to evaluate the chemical potentials of compounds, and of ions in solution, it is necessary to define the following standard states:

1. The standard chemical potentials of the elements in the form that they are normally stable at the temperature and pressure under consideration are given an arbitrary zero

$$\mu^\circ (\text{element}) = 0 \quad \dots (20.153)$$

2. In the case of ions in solution, and of gases, the chemical potential will depend upon concentration and pressure, respectively. For ions in solution the standard chemical potential of the hydrogen ion, at the temperature and pressure under consideration, is given an arbitrary value of zero at a specified concentration

$$\mu_{\text{H}^+}^\circ = 0, \text{ when } a_{\text{H}^+} = 1 \quad \dots (20.154)$$

where a_{H^+} is the activity of the hydrogen ion.

Standard chemical potentials for ions and compounds are given in Chapter 21, Table 21.5.

Activity

The chemical potential of the hydrogen ion, or of any other ion, will vary with activity

$$\mu_i = \mu_i^\circ + RT \ln a_i \quad \dots (20.155)$$

where the activity a_i is a thermodynamic quantity that is related to the concentration of the ion and takes into account the fact that a solute in solution does not behave ideally at finite concentrations; only at infinite dilution will $a_i = c_i$ numerically, where c_i is the concentration (mol kg^{-1} , mol m^{-3} or mol dm^{-3}).

Substituting for $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, $T = 298 \text{ K}$ and using the identity $\ln x = 2.303 \log x$, equation 20.155 can be expressed as

$$\mu_i = \mu_i^\circ + 5710 \log a_i \quad \dots (20.156)$$

A similar equation is applicable to a gas, but the pressure of the gas p_g (or more strictly its fugacity) replaces the activity of the ion:

$$\mu_g = \mu_g^\circ + 5710 \log (p_g/p^\circ) \quad \dots (20.157)$$

where p° refers to a standard pressure of 1 atm or $1.01325 \times 10^5 \text{ Pa}$ (pascals). For a non-dissociating solute (e.g. urea)

$$a = \gamma c/c^\circ \quad \dots (20.158)$$

where γ is the activity coefficient ($\gamma \rightarrow 1$ as $c \rightarrow 0$) and c° is the concentration in the standard state.

For a 1-1 electrolyte (NaCl) a similar procedure may be adopted, but in this case not only do the constituent ions (Na^+ and Cl^-) become more ideal in behaviour as the concentration decreases, but also the electrolyte becomes more completely dissociated into ions. It is not possible to determine indi-

vidual ionic activity coefficient, since anions and cations cannot be studied in the absence of one another. Thus for a 1-1 electrolyte equation 20.155 is written

$$\mu = \mu^\circ + 2RT \ln a_{\pm} = \mu^\circ + 2RT \ln (\gamma_{\pm} c / c^\circ) \quad \dots (20.159)$$

where a_{\pm} is the mean ionic activity and γ_{\pm} is the mean activity coefficient, and $\gamma_{\pm} \rightarrow 1$ when $c \rightarrow 0$. More complex relationships are required for unsymmetrical electrolytes such as Na_2SO_4 , $\text{La}_2(\text{SO}_4)_3$, TiCl_4 , etc.

At sufficiently low ionic strengths the activity coefficient of each electrolyte in a mixture is given by the Debye-Hückel limiting law

$$\log \gamma_{\pm} = - |z_+ z_-| A \sqrt{I} \quad \dots (20.160)$$

where I the ionic strength is defined as

$$I = \frac{1}{2} \sum c_i z_i^2 \quad \dots (20.161)$$

and z_+ , z_- are the valencies of the cation and anion (NaCl is a 1-1 electrolyte, Na_2SO_4 a 2-1 electrolyte, $\text{La}_2(\text{SO}_4)_3$ a 2-3 electrolyte, etc.) and A is a constant which is $0.51 \text{ mol}^{-\frac{1}{2}} \text{ kg}^{\frac{1}{2}}$ for water at 25°C (c_i is in mol kg^{-1}).

Units It should be noted that in the S.I. the activity of a solute is defined with reference to a standard state, i.e. an ideal solution of molality 1 mol kg^{-1} . Thus the relative activity of a metal ion in solution is given by

$$a_{M^{z+}} = \frac{m_{M^{z+}}}{m^\circ} \gamma_{M^{z+}} \quad \dots (20.162)$$

where $m^\circ = 1 \text{ mol kg}^{-1}$, $m_{M^{z+}}$ is in mol kg^{-1} and $\gamma_{M^{z+}}$ is dimensionless. It follows that the relative activity is dimensionless, although units such as mol kg^{-1} , g ion litre^{-1} , etc. are still being used (see below).

Gibbs-Duhem Equation

The Gibbs free energy change of a system will depend not only on temperature and pressure but upon the chemical potentials of the species involved, and this statement may be expressed in the form of the partial differential

$$dG + \left(\frac{\partial G}{\partial T} \right)_{p, n_1, n_2, \dots} dT + \left(\frac{\partial G}{\partial p} \right)_{T, n_1, n_2, \dots} dp + \mu_1 dn_1 + \mu_2 dn_2 \quad \dots (20.163)$$

and combining with equation 20.148 and equation 20.149

$$dG = -SdT + Vdp + \sum \mu_i dn_i \quad \dots (20.164)$$

For a process carried out under isothermal and isobaric conditions

$$(dG)_{T, p} = \sum \mu_i dn_i \quad \dots (20.165)$$

and integration of this equation for a system of given chemical composition gives

$$G_{T, p, n} = \sum n_i \mu_i \quad \dots (20.166)$$

General differentiation of this equation gives

$$dG_{T, p} = \sum (n_i d\mu_i + \mu_i dn_i) \quad \dots (20.166a)$$

Since at equilibrium $(dG)_{T,p,n}$ is zero, it follows from equation 20.165 that

$$\sum n_i d\mu_i = 0 \quad \dots (20.167)$$

which is referred to as the Gibbs-Duhem equation.

For a binary solution of say A and B

$$n_A d\mu_A = -n_B d\mu_B \quad \dots (20.168)$$

and since

$$\mu_i = \mu_i^\circ + RT \ln a_i \quad \dots (20.169)$$

then

$$d\mu_i = RT d \ln a_i \quad \dots (20.170)$$

and hence

$$n_A d \ln a_A = -n_B d \ln a_B \quad \dots (20.171)$$

The Gibbs-Duhem equation is extremely important in solution chemistry and it can be seen from equation 20.171 that it provides a means of determining the activity of one component in a binary solution providing the activity of the other is known.

Spontaneity of a Reaction

An isothermal reaction can proceed spontaneously only if the total Gibbs free energy of the system decreases, i.e. the free energy of the reactants must be greater than the free energy of the products. For a reaction



$$\Delta G = \sum \mu_{\text{products}} - \sum \mu_{\text{reactants}} \quad \dots (20.172a)$$

where ΔG is the change in free enthalpy. It follows that if $\Delta G < 0$ the reaction will tend to proceed spontaneously in the direction shown; if $\Delta G > 0$ the reaction will tend to proceed spontaneously in the reverse direction; if $\Delta G = 0$ the system will be at equilibrium and will not have any tendency to proceed in either direction.

Thus for a spontaneous reaction

$$\Delta G = (c\mu_C + d\mu_D) - (a\mu_A + b\mu_B) < 0 \quad \dots (20.173)$$

and if all substances are in their standard state

$$\Delta G = (c\mu_C^\circ + d\mu_D^\circ) - (a\mu_A^\circ + b\mu_B^\circ) < 0 \quad \dots (20.174)$$

Reversible Cells

By definition

$$\Delta G = -zFE \quad \dots (20.175)$$

where E (the reversible e.m.f.) is the intensity factor in the energy term and zF (the total charge per mole of ions involved in the reaction) is the capacity factor. If the activities of the reactants and products are fixed E will be a

constant, and if $a_A = a_B = a_C = a_D = 1$ is taken as the standard state then

$$\Delta G^\circ = -zFE^\circ \quad \dots (20.176)$$

where ΔG° is the standard free enthalpy change and E° is the standard e.m.f., which is a constant for a given equilibrium at constant T .

Substituting $-zFE$ for ΔG (equation 20.176) in equation 20.151 gives

$$\Delta H = -zFE + zFT \left(\frac{\partial E}{\partial T} \right)_p \quad \dots (20.177)$$

which provides an accurate method of evaluating ΔH and ΔS (equation 20.151) from the e.m.f. of a reversible cell and the coefficient of the change of e.m.f. with temperature at constant p , since

$$-T \left(\frac{\partial(\Delta G)}{\partial T} \right)_p = zFT \left(\frac{\partial E}{\partial T} \right)_p = T\Delta S \quad \dots (20.177a)$$

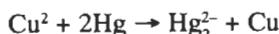
From equation 20.172a

$$\Delta G^\circ = \sum v_i \mu_i^\circ \quad \dots (20.178)$$

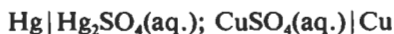
where v_i is the number of each of the ions or molecules involved in the equilibrium; combining equations 20.176 and 20.178

$$E^\circ = \frac{\sum v_i \mu_i^\circ}{zF} = - \frac{\sum v_i \mu_i^\circ}{96\,500z} \quad \dots (20.179)$$

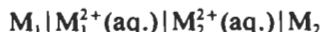
Equations 20.176 and 20.179 emphasise the essentially thermodynamic nature of the standard equilibrium e.m.f. of a cell or the standard equilibrium potential of a half-reaction E° , which may be evaluated directly from e.m.f. measurements of a reversible cell or indirectly from ΔG° , which in turn must be evaluated from the enthalpy of the reaction and the entropies of the species involved (*see* equation 20.147). Thus for the equilibrium $\text{Cu}^{2+} + 2e \rightleftharpoons \text{Cu}$, the standard electrode potential $E_{\text{Cu}^{2+}/\text{Cu}}^\circ$, and hence $\mu_{\text{Cu}^{2+}}^\circ$, can be determined by an e.m.f. method by harnessing the reaction



which can be represented by a cell without a liquid junction (or liquid junction potential)



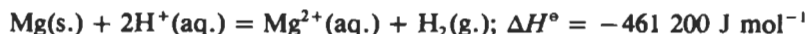
in which $|$ represents the phase boundaries. When a cell has a liquid junction the latter is represented by $||$ as in the cell



Although in certain cells the liquid junction can be eliminated by appropriate choice of electrolyte solution, this is not always possible. However, the liquid junction potential can be minimised by the use of a salt bridge (a saturated solution of KCl of about 4.2 M), and the liquid junction potential is then only 1–2 mV; this elimination of the liquid junction potential is indicated by $||$.

The standard electrode potential of M^{2+}/M can be evaluated accurately and conveniently providing it forms a reversible electrode and can be

coupled with a reference electrode to form a reversible cell. However, a number of M^{z+}/M systems do not conform to this criterion, and calorimetric methods must be used to evaluate ΔH° and ΔS° , and hence ΔG° , from which E° can be calculated. Thus in the case of the $\text{Mg}^{2+}(\text{aq.})/\text{Mg}$ equilibrium, the enthalpy change during the dissolution of the metal in dilute acid at 25°C is determined from the reaction



and the standard entropy change ΔS° is evaluated from the standard partial molar entropies of the reactants and products

$$\begin{aligned}\Delta S^\circ &= S^\circ(\text{Mg}^{2+}) + S^\circ(\text{H}_2) - S^\circ(\text{Mg}) + 2S^\circ(\text{H}^+) \\ &= -43.3 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

Since

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ \Delta G^\circ &= -461\,200 - (298 \times -43.3) \\ &= -448\,300 \text{ J mol}^{-1} \text{ at } 298 \text{ K}\end{aligned}$$

$$\therefore E^\circ_{\text{reaction}} = \frac{-\Delta G^\circ}{zF} = \frac{-448\,300}{2 \times 96\,500} = -2.3 \text{ V}$$

and since $a_{\text{H}^+} = p_{\text{H}_2} = 1$, $E^\circ_{\text{Mg}^{2+}/\text{Mg}} = -2.3 \text{ V}$

Chemical Potentials and Equilibrium

The relationship between the change in free energy ΔG and the equilibrium constant K is given by the van Hoff isotherm

$$\Delta G = -RT \ln K + RT \ln Q \quad \dots (20.180)$$

$$\text{and from equation 20.172 } K = \frac{a_{\text{C}}^c a_{\text{D}}^d}{a_{\text{A}}^a a_{\text{B}}^b} \quad \dots (20.181)$$

and a denotes the equilibrium activity of the component and Q is the activity quotient. Note that the activities of the products are in the numerator and activities of reactants in the denominator.

Equation 20.180 shows that ΔG is dependent on K and on any arbitrary activity of reactants and products that may be introduced into the equation. When the reactants and products are in their standard states

$$a_{\text{A}} = a_{\text{B}} = a_{\text{C}} = a_{\text{D}} = 1 \text{ and } \ln Q = 0 \quad \dots (20.182)$$

hence from equation 20.176

$$\Delta G = \Delta G^\circ = -RT \ln K \quad \dots (20.183)$$

$$\therefore \Delta G^\circ = -RT \ln K = -zFE^\circ \quad \dots (20.184)$$

$$\text{and } E^\circ = \frac{RT}{zF} \ln K = \frac{0.0591}{z} \log K \quad \dots (20.185)$$

since at 25°C the term $2.303 RT/F = 2.303 \times 8.314 \times 298/96\,500 = 0.0591 \text{ V}$. Combining equations 20.175 and 20.180

$$E = \frac{RT}{zF} \ln K - \frac{RT}{zF} \ln Q \quad \dots (20.186)$$

and from equation 20.185

$$E = E^\circ - \frac{0.0591}{z} \log Q = E^\circ - \frac{0.0591}{z} \log \frac{a_C^c a_D^d}{a_A^a a_B^b} \quad \dots (20.187)$$

which shows how the equilibrium potential E is dependent on the standard electrode potential E° , a constant for a given equilibrium, and the activities of reactants and products. Equation 20.187 is termed the *Nernst* equation and is applicable only when the system is reversible.

Since $\Delta G^\circ = \sum \nu_i \mu_i^\circ = -RT \ln K \quad \dots (20.188)$

$$\log K = -\frac{\sum \nu_i \mu_i^\circ}{5.710} \text{ at } 25^\circ\text{C} \quad \dots (20.189)$$

Thus the equilibrium constant K can be evaluated from standard electrode potential E° or from the standard chemical potentials μ° .

The importance of the Gibbs free energy and the chemical potential is very great in chemical thermodynamics. Any thermodynamic discussion of chemical equilibria involves the properties of these quantities. It is therefore worthwhile considering the derivation of equation 20.180 in some detail, since it forms a prime link between the thermodynamics of a reaction (ΔG and ΔG°) and its chemistry.

From the defining equations of H (equation 20.131) and G (equation 20.146) differentiation gives

$$dH = dU + pdV + Vdp \quad \dots (20.190)$$

and

$$dG = dH - TdS - SdT \quad \dots (20.191)$$

In addition, application of the first and second laws (equations 20.128 and 20.138) gives

$$dU = TdS - pdV \quad \dots (20.192)$$

Combination of these gives

$$dG = Vdp - SdT \quad \dots (20.193)$$

This equation is particularly important, because by carrying out a process isothermally ($dT = 0$), the change in the value of G can be related to the volume and pressure change alone; both of these quantities are controllable and measurable. Thus, for isothermal processes,

$$dG = Vdp \quad \dots (20.194)$$

It remains only to integrate this expression. To do this we apply initially the equation for n moles of an ideal gas

$$V = \frac{nRT}{p} \quad \dots (20.195)$$

so that

$$dG = nRT \int \frac{1}{p} dp \quad \dots (20.196)$$

Integration of this requires a limit to be defined. The limit is taken simply as follows. We define a standard pressure p° at which the Gibbs free energy has a standard value G° . We have thereby defined a standard state for this component of the system: a standard temperature too, is implicit in this since the above equations are treated for constant temperature.

Integration of equation 20.196 now gives

$$G = G^\circ + nRT \ln \frac{p}{p^\circ} \quad \dots (20.197)$$

If only one mole of the gas is considered, the quantity G is called the chemical potential, μ , or the partial molar free energy. In this case $n = 1$, and equation 20.197 becomes

$$\mu = \mu^\circ + RT \ln \frac{p}{p^\circ} \quad \dots (20.198)$$

Note that the standard state has simply to be defined; there is no *a priori* reason why it should have any particular value, save for the fact that it might as well be a convenient value. A pressure of 1 atmosphere is commonly adopted. We can thus abbreviate the equation to

$$\mu = \mu^\circ + RT \ln p \quad \dots (20.199)$$

provided the pressure of the gas, p , is expressed in atmospheres, if the standard pressure has a numerical value of 1 atmosphere. But note that the term inside the logarithm is actually dimensionless because of the *implicit* p° .

If the gas is not ideal, so that the ideal gas equation cannot be used, we replace the pressure p in equations 20.198 and 20.199 by the fugacity, f , such that the ideal gas equation still holds if the pressure p is replaced by the fugacity, an effective pressure, when the real pressure is p . This form is most convenient because of the numerous ways in which non-ideality can be expressed, and we note that the fugacity is related to, but not necessarily proportional to the pressure. We can express the fugacity as a function of the pressure by introducing the fugacity coefficient, γ_p , as $f = \gamma_p p$, which then replaces p in equation 20.199 for the non-ideal case. The value of γ_p tends to unity as the gas behaves more ideally, which means as the pressure decreases.

Consider now, a simple gas phase (with ideal gases) reaction



For each component, we may write equation 20.198. The free energy change, ΔG for the reaction is then given by

$$\begin{aligned} \Delta G &= \mu_C - \mu_B - \mu_A \\ &= \mu_C^\circ - \mu_B^\circ - \mu_A^\circ + RT \ln \frac{p_C}{p^\circ} - RT \ln \frac{p_B}{p^\circ} - RT \ln \frac{p_A}{p^\circ} \end{aligned}$$

$$= \Delta G^\circ + RT \ln \frac{\frac{p_C}{p_C^\circ}}{\frac{p_B}{p_B^\circ} \frac{p_A}{p_A^\circ}} \quad \dots (20.201)$$

Again, we define the standard state for a gas as 1 atmosphere, ie $p_A^\circ = p_B^\circ = p_C^\circ = 1$ atmosphere, so that equation 20.201 becomes

$$\Delta G = \Delta G^\circ + RT \ln \frac{p_C}{p_B p_A} \quad \dots (20.202)$$

Now, since ΔG is the driving force for the reaction to proceed, equilibrium is represented by the condition that $\Delta G = 0$. Thus the value of ΔG° is given by

$$\begin{aligned} \Delta G^\circ &= -RT \ln \frac{\frac{p_C^\epsilon}{p_C^\circ}}{\frac{p_B^\epsilon}{p_B^\circ} \frac{p_A^\epsilon}{p_A^\circ}} \\ &= -RT \ln \frac{p_C^\epsilon}{p_B^\epsilon p_A^\epsilon} \quad \dots (20.203) \end{aligned}$$

where the superscript ϵ refers to the pressure of the particular component *when the reaction is at equilibrium*. It will be recognised that the term inside the logarithm in equation 20.203 is the equilibrium constant for the reaction. This relationship (together with equation 20.202) is extremely important because it links the thermodynamics with the chemistry. We have derived the fact that ΔG° is simply another way of expressing the equilibrium constant for the reaction. It is important once again to bear in mind that the term inside the logarithm is actually dimensionless: each pressure is the ratio of the pressure to the standard pressure (expressed in the same units). Thus the equilibrium constant is also strictly a dimensionless quantity. Although units are often quoted for the equilibrium constant K for the reaction (they would be atmospheres⁻¹ in the above example), units are of course inconsistent with the exponentiation of equation 20.203, for which

$$K = \frac{p_C^\epsilon}{p_B^\epsilon p_A^\epsilon} = \exp - \frac{\Delta G^\circ}{RT} \quad \dots (20.204)$$

and the exponential term is always dimensionless. Citing of units for K (sometimes called K_p since it is a ratio of pressures as defined above) is really a method of telling one's audience what the standard states really are. Thus we could for example, consider 1 pascal of pressure as the standard state instead of 1 atmosphere. It would equally be possible to use the concentration of the gas, since the ideal gas equation contains the term n/V which is the concentration (in say, mol dm⁻³), for which the standard state could be 1 mol dm⁻³. This does not of course change the reaction, but it does change the numerical value of K and correspondingly the numerical value of ΔG° . It is not common to do this in gas phase chemistry – the usual standard state for the gas is 1 atmosphere. However, it is important

to understand the principle of it, particularly in corrosion and electrochemistry, since electrochemical systems incorporate not only gases, but solids and solutions, the latter comprising solutes and a solvent. We can now write

$$\Delta G = -RT \ln K + RT \ln \frac{p_C}{p_A p_B} \quad \dots (20.205)$$

Note that the term inside the second logarithm is *not* the equilibrium, unless the reaction is in equilibrium (for which $\Delta G = 0$). These pressures are the actual pressures used for the reaction, and the equation essentially describes the fact that the driving force for the reaction (as written) is represented by the excess pressure quotient of the reaction over and above equilibrium.

All the above deals with gases and gas phase processes. We now turn to non-gaseous components of the system. There are many ways of expressing this. Probably the simplest is to consider an ideal solution of a solute in a solvent. If the solution is ideal, the vapour pressure of the solute is proportional to its concentration, and we may write $p = kc$, where c is the concentration and k is the proportionality constant. Similarly, $p^\circ = kc^\circ$, which expresses the fact that the standard pressure is related to a standard concentration. Thus we may write from equation 20.198 for a particular component

$$\mu = \mu^\circ + RT \ln \frac{c}{c^\circ} \quad \dots (20.206)$$

This formulation now eliminates the need for a pressure entirely and replaces it by the concentration and a standard concentration. As defined above, the standard concentration is that concentration which gives rise to the standard pressure p° . However, we defined the original standard pressure arbitrarily as 1 atmosphere. We can equally validly redefine the standard concentration of the solute as 1 mol dm⁻³ of solution (unit molar or 1 M), or 1 mol kg⁻¹ of solvent (unit molal or 1 m). This in essence redefines the standard pressure, but that is of little consequence, since in corrosion and electrochemistry we are usually concerned with concentrations in solution (as an electrolyte in water, for example), and with concentrations of metal in an alloy. Moreover, because the value of k may be different for different components of the system, from the point of view of the gas pressures, we may be assigning different standard states for different gases. But that does not matter either, since we are free to define the standard states in any way we choose, and we are now interested in solution components, and not gases. Thus for example, unit concentration of hydrochloric acid (say 1 m) is a far more convenient standard state than that concentration which would equilibrate with a vapour pressure of 1 atmosphere. However, there is an added complication, already met with gases, and that is that many solutions are not ideal. So far the derivation has still been in terms of ideal solutions, because we assumed that the pressure is proportional to the concentration; hence the constant k used above. Handling of this is analogous to the non-ideal gas. We define a new term, the activity a , of the component which replaces the concentration in equation 20.206. Thus

$$a = \gamma \frac{c}{c^\circ} \quad \dots (20.207)$$

and thence for a non-ideal component

$$\mu = \mu^\circ + RT \ln \frac{\gamma c}{c^\circ} \quad \dots (20.208)$$

where c and c° are the concentration and standard concentration expressed as molalities, and γ is the activity coefficient. We are here defining the standard concentration as 1 mol solute per kg of solvent. This simply means that we are fixing the value of the chemical potential of the component as μ° when the concentration is the standard value. Note that the activity and the activity coefficient are dimensionless, and a defined standard state is implied.

But that is not all. For dilute solutions, the solvent concentration is high (55 mol kg⁻¹) for pure water, and does not vary significantly unless the solute is fairly concentrated. It is therefore common practice and fully justified to use unit mole fraction as the standard state for the solvent. The standard state of a close up pure solid in an electrochemical reaction is similarly treated as unit mole fraction (sometimes referred to as the pure component); this includes metals, solid oxides etc.

Exactly analogously then, to the gas phase reaction above, the value of ΔG and ΔG° can be formulated. Thus for the following reaction, for example:



ΔG is given by

$$\Delta G = \Delta G^\circ + RT \ln \frac{\frac{\gamma_M c_M}{c_{MO}^\circ} \left(\frac{\gamma_H c_H}{c_H^\circ} \right)^2}{\frac{\gamma_M c_M}{c_{MO}^\circ} \frac{\gamma_w c_w}{c_w^\circ}} \quad \dots (20.210)$$

where the subscripts MO , H , M , and w refer to the MO , H^+ , M^{2+} and H_2O components respectively. ΔG° is derived from the equilibrium activities as in equation 20.203, but using the appropriate concentration terms instead of pressure terms. Note that the equilibrium constant and the activity quotient in the above equation are again strictly dimensionless. Although dimensions are often quoted for K (sometimes called K_c) as described above, (for reaction 20.204 this would be mol kg⁻¹ or mol dm⁻³) these are really simply an expression of the standard states involved. Now, the standard state of the solid component (MO) and the solvent (H_2O) are defined by convention as the pure components (unit mole fraction). If the solution is dilute, $c_w \approx c_w^\circ$ and $\gamma_w = 1$. Thus the components of the equation above involving MO and H_2O are both unity. In addition, if we define the standard states of the dissolved ions as 1 M, then the relationship becomes the more familiar

$$\Delta G = \Delta G^\circ + RT \ln \frac{\gamma_H^2 c_H^2}{\gamma_M c_M} \quad \dots (20.211)$$

Note that if the water in the reaction is not of unit mole fraction (or nearly so), then its activity would have to be incorporated into equation 20.211. This could for example be in a mixed water/methanol solution. The water

concentration would then be expressed as unit mole fraction, and, for accuracy its activity coefficient relative to pure water (the standard state) would need to be known. The same is true if one of the reactants is a metal (whose standard state is the pure metal, of unit mole fraction), but the reactant is in alloy form. In summary, it is common in electrochemical reactions to adopt the following standard states. For solid components and for the solvent, the standard state is unit mole fraction. For dissolved components (such as ions) the standard state is 1 mol solute per kg of solvent, or 1 mol solute per dm³ of solution. For gas phase components the standard state is 1 atmosphere pressure.

Sign Convention for Equilibrium e.m.f.s and Potentials

For ions in solution the standard reference state is the hydrogen ion whose standard chemical potential at $a_{\text{H}^+} = 1$ is given an arbitrary value of zero. Similarly for pure hydrogen at $p_{\text{H}_2} = 1$ atm, $\mu_{\text{H}_2}^\circ = 0$. Thus for the $\text{H}^+/\frac{1}{2}\text{H}_2$ equilibrium (equation 20.179)

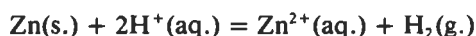
$$E^\circ = -\frac{\sum v_i \mu_i}{zF} = 0.00 \text{ V} \quad \dots (20.212)$$

and the standard hydrogen electrode (S.H.E.) is taken as the reference electrode for all other equilibria.

For a cell the equilibrium must be written in the direction in which it proceeds spontaneously, and under these circumstances

$$\Delta G < 0, \text{ and } E > 0$$

i.e. the e.m.f. of the cell will be positive. Thus for the equilibrium between Zn and H^+ the reaction is written



and if $a_{\text{H}^+} = a_{\text{Zn}^{2+}} = a_{\text{H}_2} = 1$, $E = E^\circ = +0.76 \text{ V}$. However, in the case of a half-reaction it is quite arbitrary as to whether the equilibrium is written as a reduction (electrons on the l.h.s.) or as an oxidation (electrons on the r.h.s.)



since both are correct. Substituting in the Nernst equation (equation 20.187) for equation 20.213a

$$E = E^\circ - 0.030 \log \frac{1}{a_{\text{Zn}^{2+}}} = E^\circ + 0.030 \log a_{\text{Zn}^{2+}} \quad \dots (20.213b)$$

and for equation 20.214a

$$E = E^\circ - 0.030 \log a_{\text{Zn}^{2+}} \quad \dots (20.214b)$$

Thus if the magnitudes of E are to be the same the signs of E° must be different, i.e. $E^\circ = -0.76 \text{ V}$ for equation 20.213b and $E^\circ = +0.76 \text{ V}$ for

equation 20.214*b*. If this convention is adopted, the respective electrode potentials become

$$E = -0.76 + 0.030 \log a_{\text{Zn}^{2+}} \quad \dots (20.213c)$$

$$E = +0.76 - 0.030 \log a_{\text{Zn}^{2+}} \quad \dots (20.214c)$$

and for any given activity of Zn^{2+} the E s will be the same in magnitude but opposite in sign.

It is now internationally accepted (Stockholm Convention) that the half-reaction must be written with the electrons on the l.h.s.:

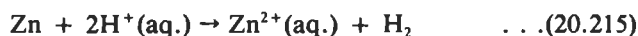


L. L. SHREIR
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20.3 The Potential Difference at a Metal/Solution Interface

Interfacial Potentials Constituting the e.m.f. of a Cell

It is quite impossible to determine the absolute potential difference across a single metal/solution interface, and the potential must be evaluated indirectly from the e.m.f. of a cell comprising the interface under consideration and another electrified interface. The e.m.f. of the cell can be determined readily by a suitable measuring device such as a potentiometer, vacuum-tube voltmeter or an electrometer, which are capable of measuring the e.m.f. with the minimum passage of electrical charge. This is essential since if a significant current is allowed to pass, the electrodes (electrified interfaces) become polarised and the e.m.f. will be less than the equilibrium value. Consider the determination of the interfacial potential at the surface of a zinc electrode in equilibrium with Zn^{2+} ions in solution. In order to determine the potential it is necessary to couple it with another electrode, and for the purpose of this discussion the equilibrium between H^+ ions in solution and H_2 gas will be chosen, i.e. the reversible hydrogen electrode in which the equilibrium between H^+ and H_2 takes place at a platinised-platinum surface. The spontaneous cell reaction will be



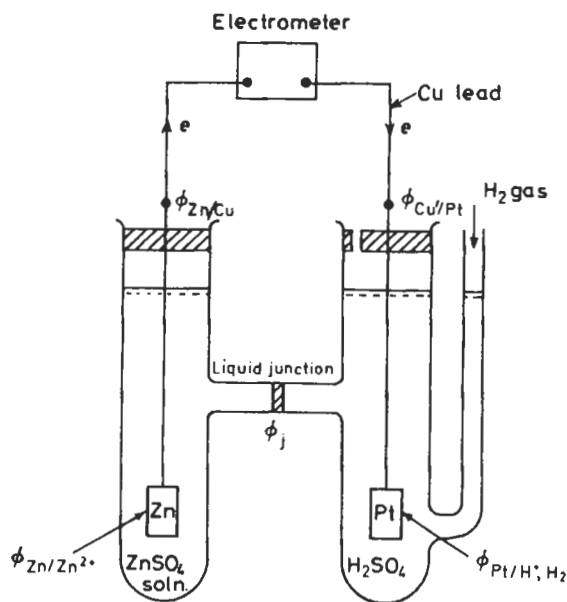
and the cell can be represented by the reversible cell



in which $|$ represents an interface.

In this cell (Fig. 20.22) the following interfaces and associated interfacial potentials may be distinguished:

1. The $\text{Zn}/\text{Zn}^{2+}(\text{aq.})$ interface and the associated interfacial potential $\phi_{\text{Zn}/\text{Zn}^{2+}}$.
2. The $\text{Pt}/\text{H}^+(\text{aq.}), \text{H}_2$ interface and the associated interfacial potential $\phi_{\text{Pt}/\text{H}^+, \text{H}_2}$.
3. The interface between the two solutions $\text{ZnSO}_4/\text{H}_2\text{SO}_4$ and the associated liquid junction potential ϕ_j .
4. The interface between the Zn electrode and the Cu lead [at which $e(\text{Zn}) \rightarrow e(\text{Cu})$] and the associated interfacial potential $\phi_{\text{Zn}/\text{Cu}}$.

Fig. 20.22 Interfacial potentials in the electrochemical cell $\text{Zn}|\text{Zn}^{2+}|\text{H}^{+}|\text{Pt}, \text{H}_2$

5. The interface between the Cu lead and the Pt electrode [at which $e(\text{Cu}') \rightarrow e(\text{Pt})$] and the associated interfacial potential $\phi_{\text{Cu}/\text{Pt}}$

Thus the e.m.f. of the cell will be the resultant of the various interfacial potentials given above, i.e.

$$E_{\text{cell}} = \phi_{\text{Zn}/\text{Zn}^{2+}} + \phi_{\text{Pt}/\text{H}^{+}, \text{H}_2} + \phi_j + \phi_{\text{Zn}/\text{Cu}} + \phi_{\text{Cu}/\text{Pt}} \dots (20.216)$$

Since the small interfacial potentials at the junctions of the electrodes and copper leads are equal and opposite, they cancel out, and if the liquid junction potential is assumed to be small, or is reduced to a negligible value by using a salt bridge, then equation 20.216 reduces to

$$E_{\text{cell}} = \phi_{\text{Zn}/\text{Zn}^{2+}} + \phi_{\text{Pt}/\text{H}^{+}, \text{H}_2} \dots (20.217)$$

At each interface the interfacial potential will depend upon the chemical potentials of the species involved in the equilibrium. Thus at the Zn/Zn^{2+} electrode there will be a tendency for zinc ions in the lattice to lose electrons and to pass across the interface and form hydrated ions in solution; this tendency is given by the chemical potential of zinc μ_{Zn} , which for pure zinc will be a constant. Similarly, there will be a tendency for hydrated Zn^{2+} ions in solution to lose their hydration sheaths, to gain electrons and to enter the lattice of the metal; this tendency is given by the chemical potential of the Zn^{2+} ions, which is related to their activity. (See equation 20.155.)

Thermodynamically

$$\phi_{\text{Zn}, \text{Zn}^{2+}} = \mu_{\text{Zn}^{2+}} - \mu_{\text{Zn}(1)} = (\mu_{\text{Zn}^{2+}}^{\ominus} + RT \ln a_{\text{Zn}^{2+}}) - \mu_{\text{Zn}(1)}^{\ominus} \dots (20.218)$$

where the superscript \ominus indicates the standard state of the species under consideration, and for pure zinc $\mu_{\text{Zn}(1)} = \mu_{\text{Zn}(1)}^{\ominus} = 0$.

Table 20.4 Classification of electrode potentials of metals

A. Reversible electrodes

Type	Characteristics	Examples
(1) $M/M_{(aq)}^{z+}$ ion (Type 1 electrode)	Metal M in solution of its cations giving an $M^{z+} \rightleftharpoons M$ exchange whose potential conforms with the Nernst equation.	Cu^{2+}/Cu , Zn^{2+}/Zn , Ag^+/Ag
(2) M /metal salt/anion (Type 2 electrode)	Metal in contact with its sparingly soluble salt MX and a soluble salt the anion X giving an $M/MX/X^-$ electrode whose potential depends on K_s of MX and the a_{X^-} .	$Hg/Hg_2Cl_2/KCl(aq.)$ $Hg/Hg_2SO_4/K_2SO_4(aq.)$ $Ag/AgCl/KCl(aq.)$
(3) Oxidation-reduction (redox)	Inert metal (normally Pt but certain other metals can act in a similar manner) in a solution containing two species that give rise to a redox system. E depends on E^\ominus of the system and the relative activities of the oxidised and reduced forms.	Quinone-hydroquinone: $C_6H_4O_2 + 2H^+ + 2e \rightleftharpoons C_6H_4(OH)_2$, which is thus pH dependent; Fe^{3+}/Fe^{2+} MnO_4^-/Mn^{2+}
(4) Metal/metal oxide	Metal filmed with oxide in a solution of OH^- giving an $M/M_xO_y/OH^-$ electrode whose potential is dependent on pH.	$Sb/Sb_2O_3/OH^-$ $Bi/Bi_2O_3/OH^-$
(5) Gas/ion	Inert electrode (usually Pt but other metals or metallic compounds may act in a similar way) in a redox system of which one component is a gas	$Pt/H_2, H^+$ $Pt/Cl_2, Cl^-$

(continued overleaf)

Table 20.4 (continued)

B. Irreversible electrodes

Type	Characteristics	Examples
(1) Steady-state potential comparable with Type 1 reversible electrode	Metal in a solution of electrolyte in which M^{z+} ions are produced by a corrosion reaction in an M^{z+}/M exchange that determines the potential.	Zn in NaCl solution Zn in dilute HCl
(2) Steady-state potential comparable with Type 2 reversible electrode	Potentials of electropositive metals that react with solution to give sparingly soluble salts of the metal.	Cu or Ag in NaCl or Ag in HCl giving an $M/MX/X^-$ type of electrode
(3) Steady-state potential comparable with Types 4 and 5 reversible electrodes	Potential of metal depends on pH of solution, although the dependence is confined to a limited range of pH and does not conform precisely to the Nernst equation.	Ni in H_2SO_4 ($Ni/H_2, H^+$) Cu in NaOH ($Cu/Cu_2O/OH^-$)
(4) Corrosion or mixed potentials:	Potential dependent on the redox potential of the solution and the kinetics of the anodic and cathodic reactions.	
(a) Active corrosion in acid solutions	Potential dependent on the kinetics of the h.e.r. on the bare metal surface.	Zn in HCl
(b) Passive metal in acid solutions	Potential is that of an oxide-filmed metal, and is dependent on the redox potential of the solution.	Stainless steel in oxygenated H_2SO_4

For a reversible cell at equilibrium the Gibbs free energy and the reversible e.m.f. E_r are related by

$$\Delta G = -zFE_r = 2FE_r \quad \dots (20.219)$$

and the interfacial potential at the Zn/Zn^{2+} electrode is given by

$$\phi_{\text{Zn}/\text{Zn}^{2+}} = E_{r,\text{Zn}} = \frac{\mu_{\text{Zn}^{2+}}^\circ - \mu_{\text{Zn}}^\circ}{2F} + \frac{RT}{2F} \ln a_{\text{Zn}^{2+}} \quad \dots (20.220)$$

The standard chemical potentials $\mu_{\text{Zn}^{2+}}^\circ$ and μ_{Zn}° are constants so that the first term on the r.h.s. can be replaced by $E_{\text{Zn}^{2+}/\text{Zn}}^\circ$, the standard electrode potential of the $\text{Zn}^{2+} + 2e = \text{Zn}$ equilibrium, and

$$\phi_{\text{Zn}^{2+}/\text{Zn}} = E_{r,\text{Zn}} = E_{\text{Zn}^{2+}/\text{Zn}}^\circ + \frac{RT}{2F} \ln a_{\text{Zn}^{2+}} \quad \dots (20.221)$$

Similarly for the $2\text{H}^+ + 2e = \text{H}_2$ equilibrium

$$\phi_{\text{H}^+/\text{H}_2} = E_{r,\text{H}} = E_{\text{H}^+/\text{H}_2}^\circ + \frac{RT}{2F} \ln \frac{a_{\text{H}^+}^2}{p_{\text{H}_2}} \quad \dots (20.222)$$

Subtracting equation 20.221 from 20.222

$$\phi_{\text{H}^+/\text{H}_2} - \phi_{\text{Zn}^{2+}/\text{Zn}} = E_{r,\text{cell}} = E_{\text{cell}}^\circ + \frac{RT}{2F} \ln \frac{a_{\text{H}^+}^2}{a_{\text{Zn}^{2+}} p_{\text{H}_2}} \quad \dots (20.223)$$

The above considerations show that the equilibrium e.m.f. of a reversible cell is determined solely by the interfacial potentials at the two electrodes constituting the cell, providing the liquid junction can be eliminated or made negligible, and under these circumstances the interfacial potentials will be related to the chemical potentials of the species involved in the equilibrium. In the case of an irreversible cell, e.g.



there will be the same number of interfacial potentials as in the reversible $\text{Zn}|\text{ZnSO}_4|\text{H}_2\text{SO}_4|\text{Pt, H}_2$ cell, but the e.m.f. of the cell cannot be treated thermodynamically.

Examples of reversible and irreversible electrodes and electrode potentials are given in Table 20.4.

Non-polarisable and Polarisable Interfaces

An ideal reversible cell is characterised by an e.m.f. that remains constant irrespective of the rate of reaction in either direction, i.e. each interface constituting the cell must be so completely non-polarisable that it resists any attempt to change its potential. Although this is impossible to achieve in practice, a number of interfaces approximate to ideality providing the rate of reaction is maintained at a very low value. These reversible electrodes (or half-cells) are used as reference electrodes for determining the potential of a single electrified interface.

At the other extreme is the completely polarisable interface for which a very small passage of charge will result in a very large change in potential.

The calomel electrode $\text{Hg}/\text{Hg}_2\text{Cl}_2, \text{KCl}$ approximates to an ideal non-polarisable electrode, whilst the $\text{Hg}/\text{aqueous electrolyte solution}$ electrode approximates to an ideal polarisable electrode. The electrical behaviour of a metal/solution interface may be regarded as a capacitor and resistor in parallel (Fig. 20.23), and on the basis of this analogy it is possible to distinguish between a completely polarisable and completely non-polarisable

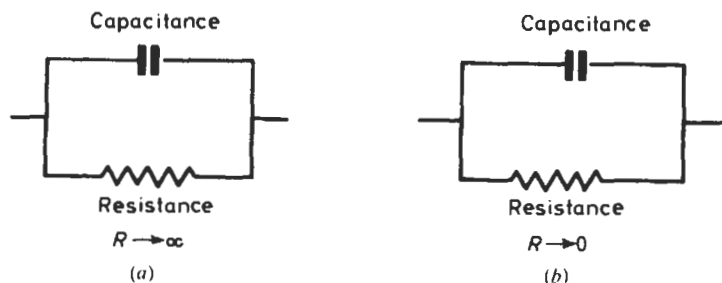


Fig. 20.23 Analogy between a metal/solution interface and a capacitance and resistance in parallel. (a) Non-polarisable electrode, e.g. Hg/KCl solution, (b) polarisable electrode, e.g. $\text{Hg}/\text{Hg}_2\text{Cl}_2, \text{KCl}$ solution

interface. The polarisable electrode will have a high resistance so that when it is connected to a source of e.m.f. the capacitor will become charged up to the value of the potential difference of the source, i.e. it will polarise. Conversely, when the resistance in parallel with the capacitor is low, charge will leak through the resistance and will thus prevent the charging up of the capacitor, i.e. it will be non-polarisable. Polarisable electrodes such as $\text{Hg}/\text{aqueous KCl}$ are used for studies of the structure of the electrical double layer, whilst non-polarisable electrodes are used as reference electrodes and for evaluating thermodynamic parameters such as the chemical potentials of ions in solution.

Thermodynamics of a Reversible Cell

If a reaction is harnessed in a reversible cell and the reaction is allowed to proceed at an infinitely slow rate (almost at equilibrium), the work energy will be a maximum and will be equal to the Gibbs free enthalpy of the reaction (see equation 20.219). The reversible e.m.f. will be the maximum e.m.f. of the cell reaction, and if the reaction is allowed to proceed reversibly at constant temperature and pressure the heat transferred between the cell and its surroundings will give the entropy change of the reaction (see equation 20.137). On the other hand, if the cell reaction is allowed to proceed irreversibly in a calorimeter, all the internal energy of the reactants will appear as heat energy and the external work will be zero (disregarding pV work). If the cell is allowed to operate irreversibly at a finite rate the work energy will decrease (the e.m.f. of the cell will be less than the reversible e.m.f.) and more heat will be transferred from the cell to the surroundings than when it operates reversibly, i.e. the entropy of the system will increase.

This can be exemplified by considering the spontaneous reaction



for which the equivalent reversible cell without a liquid junction, and hence without a liquid junction potential, can be represented by



When the concentration of ZnCl_2 is 0.5 M the e.m.f. of the cell at 298 K is found to be 1.015 V, whilst the temperature coefficient of the cell is 0.00049 V K^{-1} . Thus the free energy change (equation 20.219) is:

$$\Delta G_{298\text{K}} = -(2 \times 1.015 \times 96\,500) = -196 \text{ kJ mol}^{-1}$$

showing that the reaction has a large tendency to proceed in the direction in which it has been written.

From equation 20.151 it is possible to calculate the enthalpy change

$$\Delta H_{298\text{K}} = -196 - \frac{298(2 \times 96\,500 \times 0.00049)}{1\,000} = -224 \text{ kJ mol}^{-1}$$

and since $\Delta H > \Delta G$ it follows that during the reversible operation of the cell heat is lost by the cell and gained by the surroundings.

Also from equation 20.149

$$\Delta S = - \left(\frac{\partial G}{\partial T} \right)_p = -zF \left(\frac{\partial E}{\partial T} \right)_p$$

$$\therefore \Delta S = -2 \times 96\,500 \times 0.00049 = -95 \text{ J K}^{-1} \text{ mol}^{-1}$$

Reference Electrodes

It is evident that it is only possible to measure the e.m.f. of a cell, and that in order to determine the potential at a single electrified interface it is necessary to assign an arbitrary potential to a specified electrified interface, which is then used as a reference for all others. The $\text{H}^+/\frac{1}{2}\text{H}_2$ equilibrium at a platinum surface has been selected for this purpose, and at $a_{\text{H}^+} = p_{\text{H}_2} = 1$ the standard equilibrium potential $E_{\text{H}^+/\frac{1}{2}\text{H}_2}^\circ$ is given an arbitrary value of 0.00 V at 25°C; at any other activity of hydrogen ions or pressure of hydrogen gas the potential of the equilibrium $\text{H}^+ + e = \frac{1}{2}\text{H}_2$ is given by

$$E = E^\circ - \frac{RT}{F} \ln \frac{p_{\text{H}_2}^{1/2}}{a_{\text{H}^+}} \quad \dots (20.224)$$

or

$$E = 0.00 + 0.059 \log a_{\text{H}^+} - 0.030 \log p_{\text{H}_2} \quad \dots (20.225)$$

The hydrogen electrode consists of an electrode of platinum foil (approximately $1 \times 1 \times 0.002 \text{ cm}$) welded to a platinum wire which is fused into a glass tube. In order to increase its catalytic activity it is platinised by making it cathodic in a solution of chloroplatinic acid (2% chloroplatinic acid in 2 N HCl); frequently lead acetate is added to the solution (0.02%) and this appears to facilitate the deposition of an even and very finely divided layer

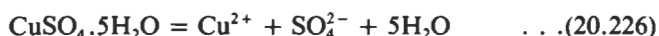
of platinum black, which has a higher catalytic activity than bulk platinum. It is immersed in an acid of known activity (1.2 M HCl gives an activity of hydrogen ion ≈ 1.0) and pure hydrogen gas is bubbled into the acid.

Although the hydrogen electrode provides a means of defining the equilibrium potentials of all other equilibria that give rise to an interfacial potential it is more convenient in practice to use other reference electrodes, e.g. Ag/AgCl, Cl^- ; Hg/Hg₂Cl₂, Cl^- ; Cu/CuSO₄, etc. which are easier to prepare and do not involve a gas/ion equilibrium. However, the hydrogen electrode is widely used in fundamental studies of electrochemistry.

Electrodes such as Cu^{2+}/Cu which are reversible with respect to the ions of the metal phase, are referred to as *electrodes of the first kind*, whereas electrodes such as Ag/AgCl, Cl^- that are based on a sparingly soluble salt in equilibrium with its saturated solution are referred to as *electrodes of the second kind*. All reference electrodes must have reproducible potentials that are defined by the activity of the species involved in the equilibrium and the potential must remain constant during, and subsequent to, the passage of small quantities of charge during the measurement of another potential.

In the case of the Cu/CuSO₄ electrode (an electrode of the first kind that is widely used for determination of the potential of steel in underground environments), the reversible equilibrium $\text{Cu}^{2+} + 2e \rightleftharpoons \text{Cu}$ determines the interfacial potential, and constancy of $a_{\text{Cu}^{2+}}$ is ensured by using a saturated solution of CuSO₄ in equilibrium with crystals of CuSO₄.5H₂O.

The difference between $E_{\text{Cu}^{2+}/\text{Cu}}^\circ = 0.337 \text{ V}$ and $E = 0.30 \text{ V}$ for the Cu/CuSO₄, saturated half-cell is due to the equilibrium



and the chemical potential of CuSO₄.5H₂O must be taken into account in evaluating the $a_{\text{Cu}^{2+}}$. At equilibrium

$$a_{\text{Cu}^{2+}} \times a_{\text{SO}_4^{2-}} = K \quad \dots (20.227)$$

and

$$\begin{aligned} \log K &= \log a_{\text{Cu}^{2+}} + \log a_{\text{SO}_4^{2-}} \\ &= \frac{\mu_{\text{CuSO}_4 \cdot 5\text{H}_2\text{O}}^\circ - \mu_{\text{Cu}^{2+}}^\circ - \mu_{\text{SO}_4^{2-}}^\circ - 5\mu_{\text{H}_2\text{O}}^\circ}{5707} \quad \dots (20.228) \end{aligned}$$

By assuming that $\mu_{\text{H}_2\text{O}}^\circ$ is the same as that for pure water, which is unlikely in this concentrated solution, and by substituting for the chemical potentials in equation 20.228, Pourbaix has calculated that

$$\log a_{\text{Cu}^{2+}} + \log a_{\text{SO}_4^{2-}} = -2.96 \quad \dots (20.229)$$

Since

$$a_{\text{Cu}^{2+}} = a_{\text{SO}_4^{2-}} \quad \dots (20.230)$$

then

$$\log a_{\text{Cu}^{2+}} = -2.96/2 = -1.48 \quad \dots (20.231)$$

which corresponds with $a_{\text{Cu}^{2+}} = 0.033$.

Substituting in the Nernst equation (equation 20.187)

$$E = 0.337 - (0.030 \times 1.48) = 0.293 \text{ V} \approx 0.30 \text{ V}$$

which is the potential of the Cu/CuSO₄, saturated reference electrode.

The Ag/AgCl, Cl⁻ electrode, which may be regarded as typical of electrodes of the second kind, consists of AgCl in contact with a soluble chloride, usually KCl. This electrode is essentially an Ag⁺ + e = Ag electrode, in which the a_{Ag⁺} is controlled by the solubility product K_s of AgCl and by the a_{Cl⁻}. Thus

$$E = E_{\text{Ag}^+/\text{Ag}}^\circ + \frac{RT}{F} \ln a_{\text{Ag}^+} \quad \dots (20.232)$$

and since

$$a_{\text{Ag}^+} \times a_{\text{Cl}^-} = \text{constant} = K_s \quad \dots (20.233)$$

at constant temperature, then

$$E = E_{\text{Ag}^+/\text{Ag}}^\circ + \frac{RT}{F} \ln \frac{K_s}{a_{\text{Cl}^-}} = E_{\text{Ag}^+/\text{Ag}}^\circ + \frac{RT}{F} \ln K_s - \frac{RT}{F} \ln a_{\text{Cl}^-} \quad \dots (20.234)$$

Taking the two constant terms on the r.h.s. of equation 20.234 as $E_{\text{Ag}/\text{AgCl}}^\circ$

$$E = E_{\text{Ag}/\text{AgCl}}^\circ - \frac{RT}{F} \ln a_{\text{Cl}^-} \quad \dots (20.235)$$

$$\text{where } E_{\text{Ag}/\text{AgCl}}^\circ = E_{\text{Ag}^+/\text{Ag}}^\circ + \frac{RT}{F} \ln K_s = 0.22233 \text{ V at } 25^\circ\text{C} \quad \dots (20.236)$$

$$\text{and } E = E_{\text{Ag}/\text{AgCl}}^\circ \text{ when } a_{\text{Cl}^-} = 1 \quad \dots (20.237)$$

Values of $E_{\text{Ag}/\text{AgCl}}^\circ$ in the range of temperature 0–95°C are available, and the Ag/AgCl, Cl⁻ electrode is probably the most accurate reference electrode for use in solutions at elevated temperatures.

It is apparent that since the electrode potential of a metal/solution interface can only be evaluated from the e.m.f. of a cell, the reference electrode used for that purpose must be specified precisely, e.g. the criterion for the cathodic protection of steel is –0.85 V (vs. Cu/CuSO₄, sat.), but this can be expressed as a potential with respect to the standard hydrogen electrode (S.H.E.), i.e. –0.55 V (vs. S.H.E.) or with respect to any other reference electrode. Potentials of reference electrodes are given in Table 21.7.

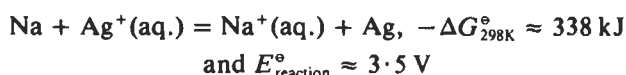
E.M.F. Series of Metals

The standard electrode potentials of $M^{z+} + ze = M$ equilibria, $E_{M^{z+}/M}^\circ$, when arranged in a table according to the sign and magnitude of the potential constitute the so-called e.m.f. series of metals. Again it should be emphasised that these are thermodynamic parameters whose magnitude and sign will depend upon the energy required to convert a metal ion in the lattice of the metal to a hydrated ion in solution. Energetically, this will involve

conversion of a metal atom in the lattice to a gaseous atom, the ionisation of the metal atom and the hydration of the metal ion to form a hydrated ion in solution. This can be illustrated by comparing the component enthalpies for transforming $\text{Na(l.)} \rightarrow \text{Na}^+(\text{aq.})$ and $\text{Ag(l.)} \rightarrow \text{Ag}^+(\text{aq.})$

	ΔH° (kJ)		ΔH° (kJ)
Sublimation			
$\text{Na(l.)} = \text{Na(g.)}$	109	$\text{Ag(l.)} = \text{Ag(g.)}$	280
Ionisation			
$\text{Na(g.)} = \text{Na}^+(\text{g.}) + e(\text{g.})$	494	$\text{Ag(g.)} = \text{Ag}^+(\text{g.}) + e(\text{g.})$	728
Hydration			
$\text{Na}^+(\text{g.}) = \text{Na}^+(\text{aq.})$	-397	$\text{Ag}^+(\text{g.}) = \text{Ag}^+(\text{aq.})$	-464
	<hr/> 206		<hr/> 544

It can be seen that ΔH° for $\text{Ag} \rightarrow \text{Ag}^+(\text{aq.})$ is much greater than that for $\text{Na} \rightarrow \text{Na}^+(\text{aq.})$ which means that silver has a much lower tendency to ionise than sodium; conversely, $\text{Ag}^+(\text{aq.})$ ions have a much greater tendency to gain electrons and become reduced to metal than $\text{Na}^+(\text{aq.})$ ions. This difference, as can be seen, is largely due to the higher sublimation energy and ionisation energy of silver compared with sodium. If the entropy change is regarded as negligible, then $\Delta H^\circ \approx \Delta G^\circ$, and for the reaction



which is in agreement with the e.m.f. evaluated from the standard electrode potential, i.e. $E_{\text{Ag}^+/\text{Ag}}^\circ = 0.799 \text{ V}$ and $E_{\text{Na}^+/\text{Na}}^\circ = -2.71 \text{ V}$.

These considerations show the essentially thermodynamic nature of $E_{M^{z+}/M}^\circ$, and it follows that only those metals that form reversible $M^{z+} + ze = M$ systems, and that are immersed in solutions containing their cations, take up potentials that conform to the thermodynamic Nernst equation. It is evident, therefore, that the e.m.f. series of metals has little relevance in relation to the actual potential of a metal in a practical environment, and although metals such as silver, mercury, copper, tin, cadmium, zinc, etc. when immersed in solutions of their cations do form reversible systems, they are unlikely to be in contact with environments containing unit activities of their cations. Furthermore, although silver when immersed in a solution of Ag^+ ions will take up the reversible potential of the Ag^+/Ag equilibrium, similar considerations do not apply to the Na^+/Na equilibrium since in this case the sodium will react with the water with the evolution of hydrogen gas, i.e. two exchange processes will occur, resulting in an extreme case of a corrosion reaction.

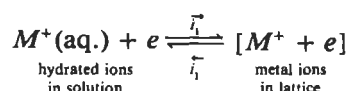
The potential of the electrified interface of a metal immersed in an aqueous solution is of fundamental importance in studying the mechanism of corrosion reactions and in corrosion testing and monitoring, and it is, therefore, of some importance to consider the factors that determine the potential of a metal in a practical environment. The determination of the potential can be achieved without difficulty, but the significance of the potential is far more complex and some of the factors that affect the potential are as follows:

1. The reversibility of the M^{z+}/M , H^+/H_2 and O_2/OH^- systems.

2. The number of possible equilibria that can occur if two or more are involved the potential is a *mixed* or *corrosion* potential.
3. The surface of the metal, i.e. film free or filmed with corrosion products.
4. The nature of the environment, i.e. composition, temperature, pressure, velocity, etc.

Reversible Potentials and Exchange Current Densities

Previous considerations have shown that the interface between two conducting phases is characterised by an unequal distribution of electrical charge which gives rise to an electrical double layer and to an electrical potential difference. This can be illustrated by considering the transport of charge (metal ions or electrons) that occurs immediately an isolated metal is immersed in a solution of its cations:



where i_1^- is the rate of the discharge (or cathodic) process and i_1^+ is the rate of the dissolution (or anodic) process. Initially and momentarily the rates of these two processes will not be equal and the one that predominates will determine the potential of the metal with respect to the solution. Figure 20.24 illustrates the situation at the metal/solution interface and it can be seen that for transfer of charge in either direction the ions involved must surmount an energy barrier which has a maximum value of E^* . Since in 20.24a the energy well for the hydrated ion is lower than that for the metal ion in the lattice, dissolution will occur at a greater rate initially than discharge, resulting in an electrical double layer in which the metal has an excess negative charge and the solution an excess positive charge. However, this situation proceeds only for an instant of time, since the double layer produces an electric field normal to the interface that rapidly reduces the *net* current to zero. At equilibrium the field produced tends to equalise the energy wells

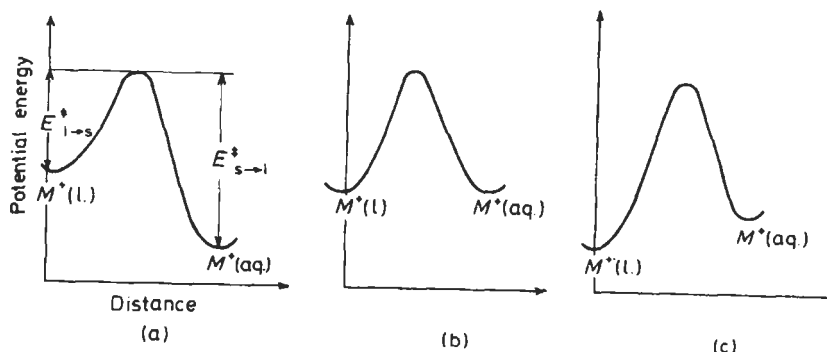


Fig. 20.24 Potential energy-distance from metal surface curves, illustrating (a) an M^+/M system in which, owing to the relative position of the energy wells, the initial ionisation reaction occurs more rapidly than the discharge reaction, resulting in an excess negative charge on the surface of the metal, (b) equilibrium at which the energy wells are approximately the same and (c) the converse of (a)

(Fig. 20.24b) and the rates of dissolution and discharge become equal. The potential is then the equilibrium potential, i.e.

$$\text{when } \vec{i} = \overleftarrow{i} = i_0, E = E_{\text{eq.}}$$

where i_0 is the equilibrium exchange current density. Similar considerations apply when the energy well for metal ion discharge is higher than that for dissolution, but at equilibrium the electrical double layer will have an excess positive charge on the metal side of the interface and an excess negative charge on the solution side (Fig. 20.24c).

A metal when immersed in a solution of its cations may take up the reversible potential corresponding with the $M^{z+} \rightleftharpoons M$ exchange process, but whether or not this occurs in practice will depend on the magnitude of its exchange current density in relation to any others that are possible due to other exchange processes in the solution under consideration. In oxygenated solution the $H^+ \rightleftharpoons H_2$ and $O_2 \rightleftharpoons OH^-$ equilibria provide possible alternatives, but the exchange current densities of these equilibria are usually small, and if i_0 for $M^{z+} \rightleftharpoons M$ is large, the potential of the metal will be determined by the latter.

Thus in the case of the Hg_2^{2+}/Hg equilibrium the exchange current density $i_{0,Hg}$ is $\approx 10^{-4} \text{ A cm}^{-2}$, whereas for the $H^+ \rightleftharpoons H_2$ equilibrium $i_{0,H} \approx 10^{-12} \text{ A cm}^{-2}$; it follows that it is quite impossible for mercury to take up the potential of the latter even in a highly purified solution, and that the potential will be dominated by the $Hg_2^{2+} \rightleftharpoons Hg$ exchange even when the concentration of mercury ions is very small and when the solution contains dissolved oxygen and trace impurities. Similar considerations apply to the $Ag/AgCl, Cl^-$ electrode and to the other M^{2+}/M equilibria that are used as reference electrodes such as Zn^{2+}/Zn , Cd^{2+}/Cd and Cu^{2+}/Cu . These systems thus provide convenient reference electrodes whose potentials are unaffected by the presence of dissolved oxygen or trace impurities or by small changes in pH. The above considerations have been confined to reversible M^{2+}/M systems, but where high accuracy is not required fairly reproducible potentials can be achieved using metal electrodes immersed directly in the solution under study. Platinum and gold electrodes have been used in this way, and a zinc electrode is widely used as a reference electrode for monitoring the cathodic protection of steel immersed in sea-water; in the case of the Zn /sea-water electrode the corrosion potential approximates very closely to the standard electrode potential of Zn^{2+}/Zn . Potentials of various reference electrodes are provided in Table 21.7.

In the case of the hydrogen electrode the metal must be immersed in a solution of hydrogen ions, and this precludes all metals that react when placed in acid solutions. Furthermore, the exchange current density must be greater than $2 \times 10^{-4} \text{ A cm}^{-2}$ as otherwise even a trace of oxygen in solution will affect the potential, and platinised-platinum ($i_{0,H} \approx 10^{-3} \text{ A cm}^{-2}$) is the most suitable metal for this purpose. Gold, iridium, rhodium and ruthenium with activated surfaces may also be used, and even silver if the solution is very highly purified. It is also interesting to note that pure nickel, coated with finely divided nickel, tends to take a potential that corresponds with the pH of a nickel plating bath even though there is a very high activity of Ni^{2+} present.

Corrosion potentials are obviously of particular importance for corrosion reactions, and have been considered in some detail in Sections 1.4–1.7.

Oxide Electrodes

Metals in practice are usually coated with an oxide film that affects the potential, and metals such as Sb, Bi, As, W and Te behave as reversible $M/M_xO_y/OH^-$ electrodes whose potentials are pH dependent; electrodes of this type may be used to determine the solution's pH in the same way as the reversible hydrogen electrode. According to Ives and Janz these electrodes may be regarded as a particular case of electrodes of the second kind, since the oxygen in the metal oxide participates in the self-ionisation of water.

Thus a reversible electrode of the type $M/MO/H^+$ must conform with the thermodynamic equilibria



and the potential will be determined by the $a_{M^{2+}}$ (equation 20.238a) and by the solubility product of the oxide (equation 20.238b), i.e.

$$K_s = a_{M^{2+}} a_{O^{2-}}$$

and since there is an equilibrium between O^{2-} ions and OH^- ions

$$K'_s = a_{M^{2+}} a_{OH^-}^2$$

where K'_s is the solubility product of the hydroxide (or oxy-hydroxide)

$$\therefore E = E_{M^{2+}/M}^\circ + \frac{RT}{zF} \ln K'_s - \frac{RT}{F} \ln a_{OH^-}$$

and since for water

$$K_w = a_{H^+} a_{OH^-}$$

$$E = E_{M^{2+}/M}^\circ + \frac{RT}{2F} \ln K'_s - \frac{RT}{F} \ln K_w + \frac{RT}{F} \ln a_{H^+} \quad \dots (20.239)$$

Since the first three terms of equation 20.239 are constant, it can be written in the form

$$E = E_{M,MO,H^+}^\circ + \frac{RT}{F} \ln a_{H^+}$$

or

$$E = E_{M,MO,H^+}^\circ - 0.059 \text{ pH}$$

which is applicable in dilute solutions in which the $a_{H_2O} \approx 1$.

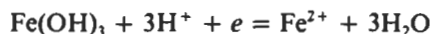
The best known of the M/M_xO_y electrodes that are used for the determination of pH are the Sb/Sb₂O₃ electrodes, but metals such as bismuth and arsenic filmed with their respective oxide act in a similar manner. Copper in alkaline solutions appears to behave as a pH-dependent Cu/Cu₂O,

OH^- electrode, whereas in chloride solutions the electrode behaves as $\text{Cu}/\text{Cu}_2\text{Cl}_2$, Cl^- whose potential depends on the a_{Cl^-} in the same way as the Ag/AgCl , Cl^- electrode.

Examples

Example 1 Derive the relationship between potential and pH for the equilibrium between $\text{Fe}(\text{OH})_3$ and $\text{Fe}^{2+}(\text{aq.})$ at 25°C . The relevant standard chemical potentials μ° in kJ are as follows: $\text{Fe}(\text{OH})_3$, -694 ; $\text{Fe}^{2+}(\text{aq.})$, -85 ; H_2O , -237 .

The equilibrium (written as a reduction) is



$$\text{and } E = E^\circ - \frac{0.059}{1} \log \frac{a_{\text{Fe}^{2+}}}{a_{\text{H}^+}^3}$$

$$\therefore E = E^\circ - 0.059 \log a_{\text{Fe}^{2+}} + 0.178 \log a_{\text{H}^+}$$

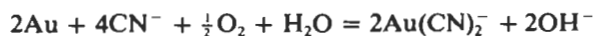
$$\begin{aligned} \therefore E^\circ &= -\frac{\sum \nu_i \mu_i^\circ}{zF} = -\frac{\sum \nu_i \mu_i^\circ}{z \times 96\,500} \times 10^3 \text{ (when } \mu^\circ \text{ is in kJ)} \\ &= -\frac{[\sum \nu_i \mu_i^\circ(\text{products}) - \sum \nu_i \mu_i^\circ(\text{reactants})]}{z \times 96\,500} \\ &= -\frac{[(-85 + 3(-237) - (-694))] \times 10^3}{1 \times 96\,500} = 1.05 \text{ V} \end{aligned}$$

$$\therefore E = 1.05 - 0.059 \log a_{\text{Fe}^{2+}} - 0.178 \text{ pH}$$

which defines the equilibrium between $\text{Fe}(\text{OH})_3$ and $\text{Fe}^{2+}(\text{aq.})$ in terms of the equilibrium potential E and pH.

Example 2 Finely divided gold is agitated with an oxygen-saturated alkali-cyanide solution of $\text{pH} = 12$ containing $10^{-2} \text{ mol dm}^{-3}$ of CN^- . Calculate the concentration of $\text{Au}(\text{CN})_2^-$ ions in solution at 25°C when the reaction is at equilibrium. The standard chemical potentials of the species involved (in kJ) are: CN^- , 165; H_2O , -237 ; $\text{Au}(\text{CN})_2^-$, 244; OH^- , -157 . Assume that $a_{\text{H}_2\text{O}} = 1$, and take $2.303 RT = 5\,710$.

The relevant equilibrium is



and from equation 20.211

$$\ln K = -\frac{\sum \nu_i \mu_i^\circ}{RT} \text{ and } \log K = -\frac{\sum \nu_i \mu_i^\circ}{5\,707}$$

$$\text{Since } \log K = -\frac{[\sum \mu_{\text{products}}^\circ - \sum \mu_{\text{reactants}}^\circ]}{5\,710}$$

$$\log K = - \frac{[(2 \times 244 + 2 \times (-157)) - \{(4 \times 165) + (-237)\}] \times 10^3}{5710}$$

$$\text{and } \log K = \frac{249 \times 10^3}{5710} \approx 43$$

$$\therefore K \approx 10^{43}$$

$$\text{Since } a_{\text{H}_2\text{O}} = p_{\text{O}_2} = 1$$

$$\frac{a_{\text{Au(CN)}_2^-}^2 \times a_{\text{OH}^-}^2}{a_{\text{CN}^-}^4} \approx 10^{43}$$

$$\text{and } a_{\text{Au(CN)}_2^-} = \left[\frac{10^{43} \times (10^{-2})^4}{(10^{-2})^2} \right]^{\frac{1}{2}} \approx 10^{19.5}$$

This high thermodynamic activity shows that gold is extremely unstable in an oxygenated cyanide solution.

Example 3 Calculate the rate (A cm^{-2}) of hydrogen evolution on platinum in an acid solution when the overpotential is (a) -0.2 V , (b) -0.300 V . Assume that $i_0 = 1 \times 10^{-4} \text{ A cm}^{-2}$, the transfer coefficient $\alpha = 0.5$ and the number of electrons involved in one act of the r.d.s $z = 1$; $\frac{RT}{F} \ln x = 0.059 \log x$.

$$\eta = \frac{RT}{z\alpha F} \ln i_0 - \frac{RT}{z\alpha F} \ln i_c$$

$$\therefore \eta = \frac{0.059}{1 \times 0.5} \log i_0 - \frac{0.059}{1 \times 0.5} \log i_c = 0.12 \log i_0 - 0.12 \log i_c$$

$$\therefore -0.2 = 0.12 \times (-4) - 0.12 \log i_c$$

$$\therefore \log i_c = \frac{-0.28}{0.12} = -2.33$$

$$\therefore i_c \approx 5 \times 10^{-3} \text{ A cm}^{-2}$$

$$\text{When } \eta = -0.300 \text{ V}$$

$$\log i_c = -\frac{0.18}{0.12} = -1.5$$

$$\therefore i_c = 3.2 \times 10^{-2} \text{ A cm}^{-2}$$

Note: when $\eta = -0.010 \text{ V}$ equation 20.72 is applicable and $i_c = (10^{-4} \times 10^{-2}/0.059 \text{ A}) = 17 \mu\text{A cm}^{-2}$.

Example 4 A metal is corroding in an oxygen-free acid of pH 1 at 25°C according to the overall reaction $M + 2\text{H}^+ = M^{2+} + \text{H}_2$. From the data given below, calculate the corrosion rate of the metal in A cm^{-2} .

Data: the equilibrium potential $E_{M^{2+}/M}^0 = -0.76 \text{ V}$ (S.H.E.) and the solution contains $a_{M^{2+}} = 10^{-2}$; $i_{0,M} = 10^{-3} \text{ A cm}^{-2}$; z (the number of electrons involved in one act of the rate-determining step) is 2 and $\alpha = 0.5$. For the hydrogen evolution reaction $i_{0,H} = 10^{-8} \text{ A cm}^{-2}$; $z = 1$ and $\alpha = 0.5$. $RT/F \ln x = 0.059 \log x$ at 25°C .

The overpotential η is defined as

$$\eta = E_p - E_r$$

where E_p is the polarised potential and E_r the reversible potential. For the cathodic reaction

$$\eta_c = \frac{0.059}{z\alpha} \log i_0 - \frac{0.059}{z\alpha} \log i_c$$

and for the anodic reaction

$$\eta_a = \frac{-0.059}{z\alpha} \log i_0 + \frac{0.059}{z\alpha} \log i_a$$

At the corrosion potential, $E_p = E_{\text{corr.}}$ and $i_c = i_a = i_{\text{corr.}}$. For the h.e.r., $E_r = -0.059$ V at pH 1. For the $M \rightarrow M^{2+}$ reaction, $E_r = -0.76 - \frac{2(0.059)}{2} = -0.8219$ V at $a_{M^{2+}} = 10^{-2}$. Therefore for the h.e.r.

$$\begin{aligned} E_{\text{corr.}} - (-0.059) &= [(0.12 \times -8) - (0.12 \log i_{\text{corr.}})] \\ E_{\text{corr.}} &= -1.02 - 0.12 \log i_{\text{corr.}} \end{aligned} \quad \dots (1)$$

Therefore for the $M \rightarrow M^{2+}$ reaction

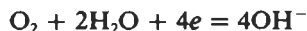
$$\begin{aligned} E_{\text{corr.}} - (-0.82) &= -[0.059 \times (-3)] + 0.059 \log i_{\text{corr.}} \\ \text{and} \quad E_{\text{corr.}} &= -0.64 + 0.059 \log i_{\text{corr.}} \end{aligned} \quad \dots (2)$$

Equating (1) and (2)

$$\begin{aligned} -1.02 - 0.12 \log i_{\text{corr.}} &= -0.64 + 0.059 \log i_{\text{corr.}} \\ -0.18 \log i_{\text{corr.}} &= 0.38 \\ \log i_{\text{corr.}} &= -\frac{0.38}{0.18} = -2.11 = -3 + 0.89 \\ i_{\text{corr.}} &\approx 8 \times 10^{-3} \text{ A cm}^{-2} \end{aligned}$$

Example 5 A stainless steel pipe is to be used to convey an aerated reducing acid at high velocity. If the concentration of dissolved O_2 is $10^{-3} \text{ mol dm}^{-3}$ ($10^{-6} \text{ mol cm}^{-3}$) calculate whether or not the steel will corrode when (a) the acid is static, (b) the acid is moving at high velocity. Assume that the critical current density for passivation of the steel in the acid is $200 \mu \text{ A cm}^{-2}$, the thickness of the diffusion layer is 0.05 cm when the acid is static and 0.005 cm when the acid flows at a high velocity; assume the diffusion coefficient of dissolved O_2 is $10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

The cathodic reaction for 1 mol of dissolved O_2 is



and hence z the number of electrons involved in each act of the reaction is 4

The limiting current density is given by

$$i_L = \frac{DzFc}{\delta}$$

and under static conditions

$$i_L = \frac{10^{-5} \times 4 \times 96\,500 \times 10^{-6}}{0.05}$$

$$\therefore i_L = 80 \mu \text{ A cm}^{-2}$$

and it follows that under flowing conditions where $\delta = 0.005 \text{ cm}$, $i_L = 800 \mu \text{ A cm}^{-2}$. Thus under static conditions $i_{\text{crit.}}$ for passivation will not be exceeded and the metal will corrode, but will passivate when the acid is flowing at a high velocity.

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*In SI units

20.4 Outline of Structural Metallurgy Relevant to Corrosion

The corrosion of metals invariably involves some kind of interaction between a metal and its environment, and in many cases the corrosion (location, form and rate) is significantly affected or even caused by some structural feature of the metal. It is essential, therefore, for the corrosion engineer to have some appreciation of the structure of metals, and an elementary survey is provided in this section which provides a basis for an account of metal structure in relation to corrosion that is the subject of Section 1.3.

This section will consider first the structure of pure metals and this will be followed by a description of the structure of alloys. In general, structural features will be discussed in order of increasing size, i.e. starting with atomic features and continuing through microscopic features to macroscopic features.

Structure of Pure Metals

A crystal may be defined as an orderly three-dimensional array of atoms, and all metals are aggregates of more or less imperfect crystals. In considering the structure of metals, therefore, it is convenient to start with the arrangement of atoms in a perfect metal crystal and then to proceed to the imperfections which are always present in the crystal structure.

Although there are many different crystal structures, some of which are rather complicated, most common metals fortunately have one of three, relatively simple structures: face-centred cubic (f.c.c.), close-packed hexagonal (c.p.h.) and body-centred cubic (b.c.c.). The unit cell (i.e. the smallest group of atoms possessing the symmetry of the crystal and which, when repeated in all directions, develops the crystal lattice) of each of these metallurgically common and important crystal structures is illustrated in Fig. 20.25; the crystal structure of each of the more important metals is given in Table 20.5. It is clear from this table that the crystal structures of some metals change with temperature, i.e. these metals are polymorphic, and this phenomenon is of very great practical significance, particularly in the case of iron, as will become apparent later.

The atoms in a metal crystal can often be satisfactorily regarded as hard spheres of radius about 10^{-10} m. A sheet of such hard balls can be

Table 20.5 Crystal structure of the more important metals

<i>Metal</i>	<i>Temperature (K)</i>	<i>Crystal structure</i>
Alkali metals	Ambient to m.p.	b.c.c.
Aluminium	Below m.p.	f.c.c.
Beryllium	Below m.p.	c.p.h.
Cadmium	Below m.p.	c.p.h.
Chromium	Below m.p.	b.c.c.
Cobalt	Below 690	c.p.h.
	690 to m.p.	f.c.c.
Copper	Below m.p.	f.c.c.
Gold	Below m.p.	f.c.c.
Iron	Below 1 180	b.c.c.
	1 180–1 665	f.c.c.
	1 665 to m.p.	b.c.c.
Lead	Below m.p.	f.c.c.
Magnesium	Below m.p.	c.p.h.
Manganese	Below m.p.	Four complex structures
Molybdenum	Below m.p.	b.c.c.
Nickel	Below m.p.	f.c.c.
Platinum	Below m.p.	f.c.c.
Silver	Below m.p.	f.c.c.
Tin	Below m.p.	Two complex structures
Titanium	Below 1 155	c.p.h.
	1 155 to m.p.	b.c.c.
Tungsten	Below m.p.	b.c.c.
Vanadium	Below m.p.	b.c.c.
Zinc	Below m.p.	c.p.h.
Zirconium	Below 1 135	c.p.h.
	1 135 to m.p.	b.c.c.

most densely and closely packed together in the configuration shown in Fig. 20.26a; such sheets or layers of atoms are therefore known as *close-packed planes*. Similarly, the directions arrowed in Fig. 20.26a are referred to as *close-packed directions*. Close-packed hexagonal and face-centred cubic crystal structures can be built up by stacking close-packed planes on top of each other in the correct sequence. Consider a sheet of eight close-packed atoms, designated by the full circles *a* in Fig. 20.26b; as shown, a second layer of four close-packed atoms, designated by the dotted circles *b*, may be laid on top of the first plane. Each of the *b* atoms 'sits' in one of the natural 'valleys' which occur between any three contiguous *a* atoms. There are now two such low-energy valleys in the plane of *b* atoms, one of which is immediately above an *a* atom and one of which is not (Fig. 20.26b). An atom placed in the former results in an *aba* stacking of three close-packed planes, while an atom placed in the latter would result in *abc* stacking. Stacking *abababab*, etc. develops the c.p.h. crystal structure while stacking *abcabcabc*, etc. develops the f.c.c. crystal structure. The b.c.c. crystal structure cannot be built up by stacking close-packed planes on top of each other.

In the f.c.c. and c.p.h. crystal structures, each atom has 12 nearest neighbours and is therefore said to have a *co-ordination number* of 12. In the non-closed-packed b.c.c. structure, on the other hand the co-ordination number is only 8. In the f.c.c. structure the four octahedral {111}* planes are close

* An account of the use of Miller indices to describe crystal planes and lattice directions is beyond the scope of this article; a very adequate treatment of this topic is, however, given in Reference 1.

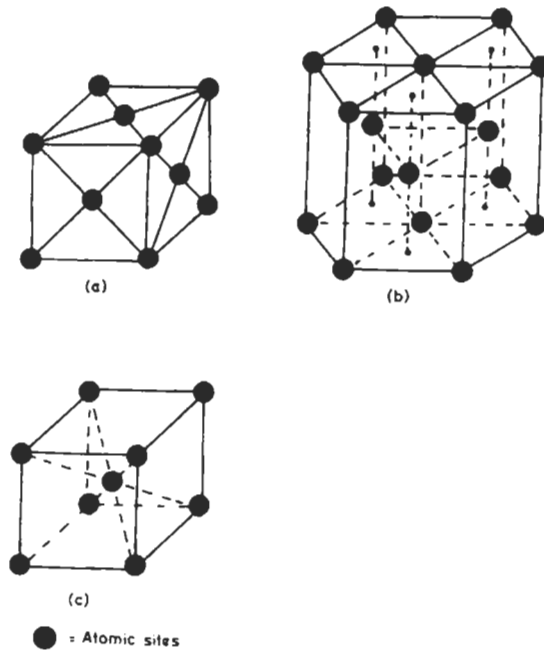


Fig. 20.25 Unit cells of (a) the face-centred cubic (f.c.c.), (b) the close-packed hexagonal (c.p.h.) and (c) the body-centred cubic (b.c.c.) crystal structures

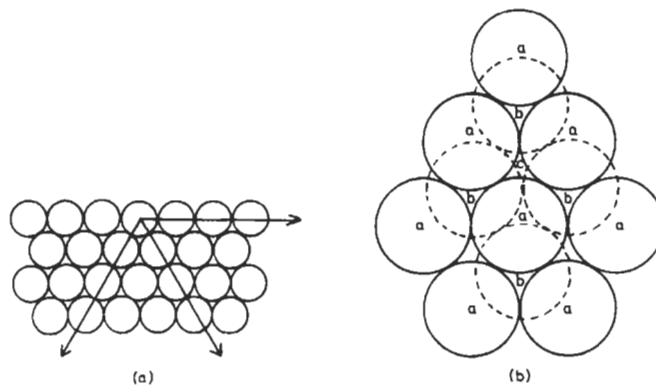


Fig. 20.26 (a) Single close-packed sheet of atoms, with the close-packed directions arrowed and (b) stacking of three close-packed planes of atoms, showing *aba* and *abc* positions

packed, while the $\langle 110 \rangle$ directions are close packed. In the c.p.h. structure on the other hand, there is only one close-packed plane, the (0001) basal plane; the $\langle 11\bar{2}0 \rangle$ directions are close packed. The different number of close-packed planes in f.c.c. and c.p.h. crystals results in the very different plastic deformation characteristics of metals with the two structures. In the b.c.c. structure, the $\langle 111 \rangle$ directions are close packed, but there are no truly close-

packed planes of the type shown in Fig. 20.26a; the planes of closest packing, however, are $\{110\}$.

In any crystal structure, the close-packed or closest-packed planes are the lowest energy planes. On all other planes, the density of atoms is lower, and the interatomic distance and the energy of the plane are greater. Contrary to intuitive expectations, the diameter of the largest holes or interstices between atoms in the close-packed f.c.c. structure is considerably greater than the diameter of the largest interstices between atoms in the non-close-packed b.c.c. structure.

Point Defects in Crystals

The smallest imperfections in metal crystals are point defects, in particular vacant lattice sites (*vacancies*) and interstitial atoms. As illustrated in Fig. 20.27a, a vacancy occurs where an atom is missing from the crystal structure

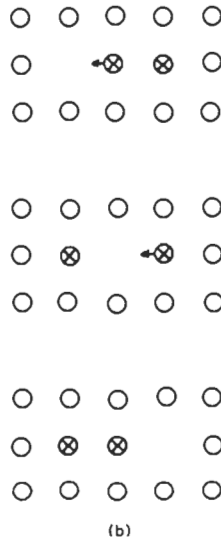
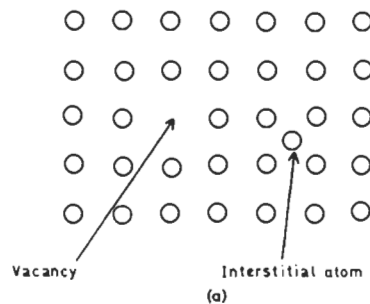


Fig. 20.27 (a) Schematic illustration of two types of point defect and (b) three stages in diffusion by the motion of a vacancy through a crystal

while an interstitial occurs when an extra atom is inserted in an interstitial site (an interstice). Vacancies and interstitials are equilibrium defects since although vacancies (and interstitials) increase the internal energy of a crystal they also increase the entropy, so the free energy of a perfect crystal is reduced by the presence of a number of point defects. The equilibrium vacancy concentration increases exponentially with temperature and typically in copper at room temperature one site in 10^{14-15} may be vacant, while at 1300K, one site in 10^{3-4} will be vacant (equivalent to 10^{17-18} vacancies per cubic millimetre). The internal energy associated with an interstitial is much greater than that associated with a vacancy; the concentration of interstitial atoms at any temperature is correspondingly very much lower than that of vacant atomic sites. Radiation damage, however, introduces many interstitials. Often a vacancy and an interstitial will be associated as a pair.

The practical importance of vacancies is that they are mobile and, at elevated temperatures, can move relatively easily through the crystal lattice. As illustrated in Fig. 20.27*b*, this is accompanied by movement of an atom in the opposite direction; indeed, the existence of vacancies was originally postulated to explain solid-state diffusion in metals. In order to 'jump' into a vacancy an adjacent atom must overcome an energy barrier. The energy required for this is supplied by thermal vibrations. Thus the diffusion rate in metals increases exponentially with temperature, not only because the vacancy concentration increases with temperature, but also because there is more thermal energy available to overcome the activation energy required for each 'jump' in the diffusion process.

Stacking Faults and Twins

In certain close-packed metals and alloys there are errors in the sequence of stacking of the close-packed planes. Thus, for example, the sequence of planes in a c.p.h. metal might be . . . abababcaba . . . , in which the region in italics is termed a *stacking fault* and represents a small volume of f.c.c. material in the c.p.h. structure. Stacking faults have an energy that is higher than that of the perfect crystal structure; however the value of the stacking-fault energy varies very widely between different metals and alloys. Stacking faults are readily visible in thin-foil transmission electron micrographs, as illustrated in Fig. 20.28 (top).

Twins are a somewhat similar form of defect. In certain metals, adjacent areas of crystal bear a mirror-image orientation relationship to each other across the twin boundary, as illustrated schematically in Fig. 20.29. The twin boundaries, like stacking faults, have a somewhat higher energy than the surrounding perfect crystal structure. Twins arise during the annealing of cold-worked f.c.c. material, during the room-temperature deformation of c.p.h. materials, and during the low-temperature (or shock) deformation of b.c.c. materials. Twins are often readily apparent on metallographic sections at relatively low magnifications, as shown in Fig. 20.28 (bottom).

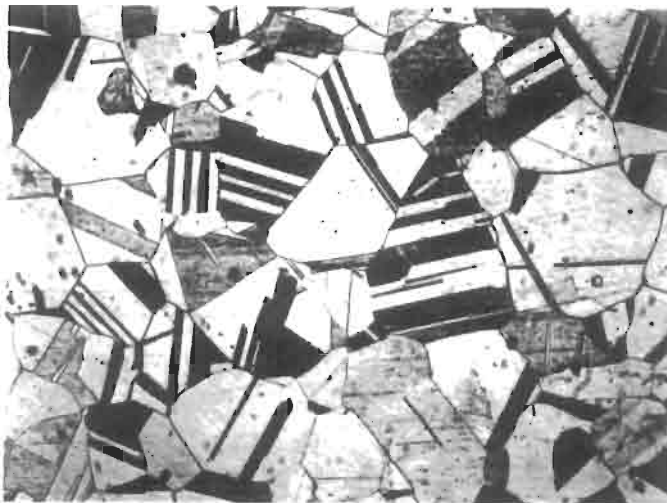
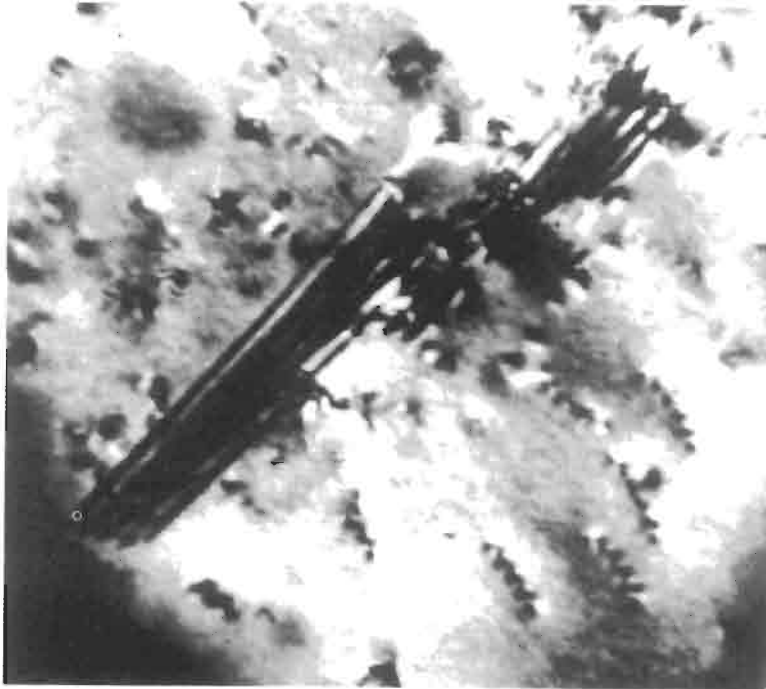


Fig. 20.28 (top) Transmission electronmicrograph showing a stacking fault and isolation dislocations in a stainless steel ($\times 70\,000$, courtesy I. Brough) and (bottom) light micrograph showing an equiaxed grain structure and twins in an annealed 70/30 brass ($\times 200$, courtesy M. Islam)

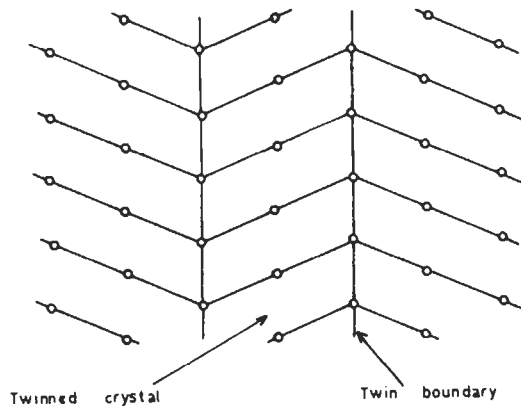


Fig. 20.29 Twinned crystal

Line Defects

Point defects, stacking faults and twins are crystalline imperfections which basically involve misalignment of single atoms or of a single plane of atoms. Line defects, or dislocations, are somewhat larger-scale imperfections involving misalignment along a line of atoms. Dislocations are extremely important defects, in that the dislocation density and dislocation interactions

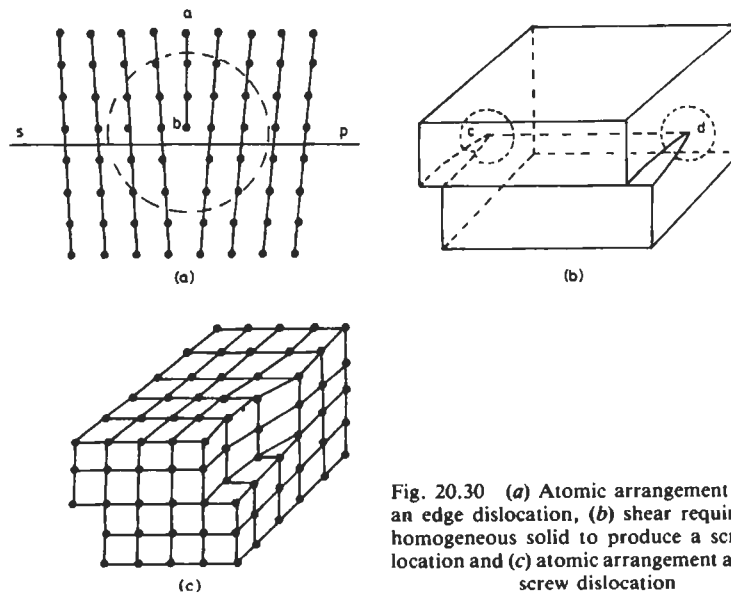


Fig. 20.30 (a) Atomic arrangement around an edge dislocation, (b) shear required in a homogeneous solid to produce a screw dislocation and (c) atomic arrangement around a screw dislocation

control to a very large extent the mechanical properties, and in particular the strength and ductility, of metals.

The simplest type of line defect is the edge dislocation, which consists of an extra half plane of atoms in the crystal, as illustrated schematically in Fig. 20.30*a*; edge dislocations are often denoted by \perp if the extra half plane *ab* is above the plane *sp*, or by Υ if it is below.

The second type of line defect is the screw dislocation, which is rather less easy to visualise. Consider, however, a block of material, half of which is sheared one interatomic distance with respect to the other half, as shown in Fig. 20.30*b*. The line *cd* then constitutes a screw dislocation; the arrangement of atoms around a screw dislocation is shown in Fig. 20.30*c*.

To a good approximation, only atoms within the dotted circles in Figs. 20.30*a* and *b* are displaced from their equilibrium position; in a real, three-dimensional crystal the diameter *d* of these circles would be very much less than the length *l* of the dislocation, i.e. the length, perpendicular to the page, of the extra half plane of atoms *ab* in Fig. 20.30*a*, or of the line *cd* in Fig. 20.30*b*. Dislocations strictly, therefore, are cylindrical defects of diameter *d* and length *l*; however, since $l \gg d$ they are referred to as *line* defects.

Movement and Interaction of Dislocations

As with vacancies, the importance of dislocations derives from the fact that they are readily mobile, in this case under the influence of applied stresses. Figures 20.31*a* to *c* illustrate the slip or glide of an edge dislocation through

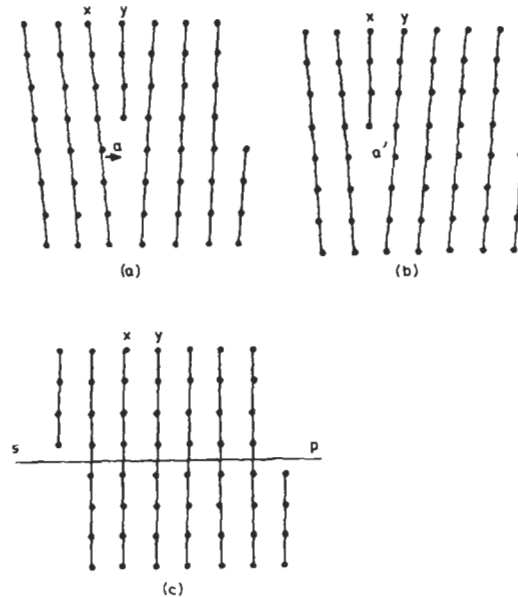


Fig. 20.31 Three stages in plastic deformation by the motion of an edge dislocation through a crystal

a crystal under the influence of a shear stress. The atom a in Fig. 20.31*a* moves, under the influence of the applied stress, to position a' in Fig. 20.31*b* and the extra half plane of atoms shifts one atomic distance to the left, from plane y to plane x . As this process continues, the dislocation moves right through the crystal, the final result, shown in Fig. 20.31*c*, being that the crystal is sheared or slipped by one interatomic distance across the slip plane sp . Each step in the movement of the dislocation (i.e. from Fig. 20.31*a* to *b*) clearly requires only a slight rearrangement of the atoms around the bottom of the extra half plane, and is therefore a low energy process; dislocations are therefore readily mobile under low applied stresses. On the other hand, to produce the slip shown in Fig. 20.31*c* from a perfect dislocation-free crystal would be a very-high-energy process requiring very high stresses. The difference between these two modes of slip is that in the latter all the bonds on the slip plane are broken at the same time, whilst in the former they are broken one at a time. The existence of dislocations was in fact postulated, long before they were observed, to account for the observation that the yield stress of metals is very much lower than that predicted by theoretical calculations. It is important to note that the crystal structure, after passage of a dislocation, is perfect and in no way misaligned. From Fig. 20.32 it is clear that the dislocation line is merely the boundary between slipped and unslipped crystal. The magnitude and direction of the slip is given by what is known as the *Burgers vector*; in a screw dislocation the Burgers vector is parallel to the line of the dislocation while in an edge dislocation it is perpendicular to it. In real crystals, dislocation lines are not straight, but are usually bowed or curved. As illustrated schematically in Fig. 20.32, such dislocations are mixed, being part screw and part edge. Slip occurs on the plane containing both the Burgers vector and the line of the dislocation. In practice, it is observed that metals slip most easily on close-packed planes and in close-packed directions, i.e. $\{111\}$ and $\langle 110 \rangle$ in f.c.c. metals and usually $\{0001\}$ and $\langle 11\bar{2}0 \rangle$ in c.p.h. metals. Since f.c.c. crystals have four close-packed $\{111\}$ planes they are generally much more ductile than c.p.h. crystals, which have only one $\{0001\}$ close-packed plane. In b.c.c. metals, slip occurs in

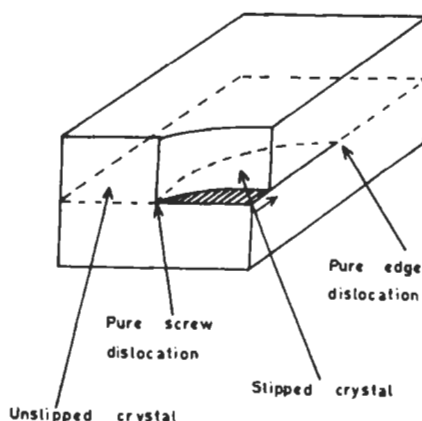


Fig. 20.32 Schematic illustration of a mixed dislocation as the boundary between slipped and unslipped crystal. The arrow shows the Burgers vector

$\langle 111 \rangle$ directions on a variety of planes. The movement of dislocations by other mechanisms, in particular by cross-slip and climb, is beyond the scope of this section.

All real metals contain dislocations; even a well-annealed metal would typically contain 10^4 – 10^6 dislocations per square millimetre, while a heavily cold-worked metal could contain up to $10^{10}/\text{mm}^2$. At first sight this is an anomaly; dislocations were postulated to account for the low yield strength of metals, and whereas an annealed material with a low dislocation density is weak, a cold-worked metal with a high dislocation density is strong. The answer lies in the fact that when the dislocation density is low, the dislocations are generally too far apart to interact with each other very often and are more free to move under the influence of a low applied stress. On the

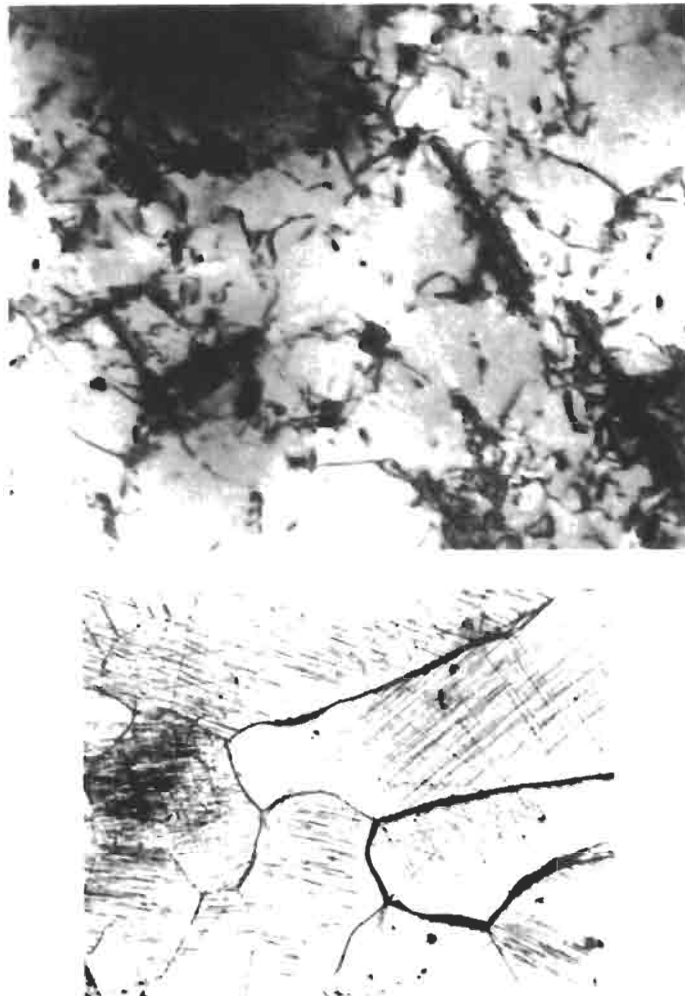


Fig. 20.33 (top) Transmission electronmicrograph showing dislocation tangles associated with precipitates in an Al-Cu-Mg-Si alloy ($\times 24\,000$, courtesy S. Blain) and (bottom) light micrograph showing slip lines in pure lead ($\times 100$)

other hand, when the dislocation density is high, the dislocations do interact and they become tangled up with each other; dislocation motion is then difficult and the material is therefore strong. The interaction of dislocations with each other and with other structural features in metals is a very complex field; it is also, however, extremely important, since it greatly affects the strength of metals.

The atomic bonds in a cylinder of material around dislocations are elastically stretched; dislocations, like other crystalline defects, are therefore high-energy regions.

Dislocations are readily visible in thin-film transmission electron micrographs, as shown in Figs. 20.28 (top) and 20.33 (top). The slip step (Fig. 20.31c) produced by the passage of a single dislocation is not readily apparent. However, for a variety of reasons, a large number of dislocations often move on the same slip plane or on bands of closely adjacent slip planes; this results in slip steps which are very easily seen in the light microscope, as shown by the slip lines in Fig. 20.33 (bottom).

Polycrystalline Metals: Grains and Grain Boundaries

So far we have regarded metals as single crystals; in fact most metals, in practice, are polycrystalline and consist of a number of crystals or grains. In a pure metal each grain will have the same crystal structure and will contain vacancies, dislocations, etc. but the crystallographic orientation of each grain will be different; in other words, in a polycrystalline metal the [111] crystallographic direction of each grain (for example) will be pointing in a different spatial direction. Typically the diameter of the grains in a coarse-



Fig. 20.34 Light micrograph showing the highly elongated grain structure of a commercial wrought high-strength precipitation-hardening Al-Zn-Mg-Cu alloy ($\times 40$, section perpendicular to the long transverse direction)

grained material might be about 0.5 mm, while that in a fine-grained metal might be about 0.005 mm. However, in certain electrodeposits the grain size is too fine to be resolved with the light microscope while at the other extreme jet-engine turbine blades about 150 mm long of nickel-base superalloy may sometimes be single crystals. The grain size of metals may be controlled by heat treatment. The grains may all be of more or less the same size and shape as in the equiaxed grain structure shown in Fig. 20.28 (bottom). Alternatively, if the metal has been heavily cold-worked, by rolling or extrusion for example, the grains may be deformed and elongated in the work direction, giving the highly directional, elongated, grain structure shown in Fig. 20.34. Although the crystallographic orientation of all the grains in a polycrystalline metal is usually different and random, occasionally the orientation of most of the grains in a piece of metal will be similar. Such preferred orientation can arise in a number of ways; it is important to note, however, that metals with elongated, columnar grain structures (Fig. 20.34) do not necessarily have preferred orientation.

However perfect the crystal structure within a grain, there will inevitably be crystallographic mismatch and imperfection where two adjacent grains meet, i.e. at grain boundaries; this region of mismatch is, however, only a few atomic diameters wide, as shown schematically in Fig. 20.35, and on metallographic sections grain boundaries only become apparent on etching. Although grain boundaries are regions of imperfection and of crystallographic mismatch, they are nevertheless quite strong and metals do not normally fail intergranularly. Indeed, grain boundaries act as barriers to the movement of dislocations and a fine-grained pure metal will normally be considerably stronger than a single-crystal or a coarse-grained material.

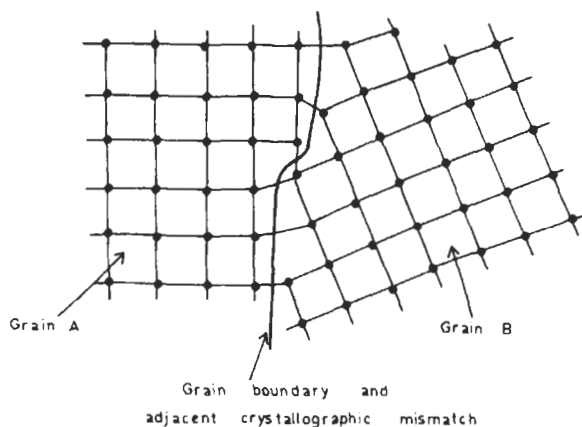


Fig. 20.35 High-angle grain boundary

A grain boundary is a planar defect in a crystal and as such has a higher energy than the surrounding crystal. By way of comparison, the free surface energy of copper is about 1 200–1 800 nJ/mm², the grain boundary energy is about 300–500 nJ/mm² while the stacking-fault energy is about 80–100 nJ/mm².

Annealing: Recovery and Recrystallisation

It must be emphasised that many of the crystalline defects already discussed are metastable, and tend to be eliminated on annealing at elevated temperatures. Thus, when a cold-worked metal is heated, the energy stored in the metal during the cold-working process is released; the dislocation tangles rearrange themselves, and the internal stresses, hardness and strength of the metal are progressively reduced. The changes occurring during this process (which is known as *recovery*) do not affect the optical microstructure of the metal. Recovery is followed at higher temperatures by recrystallisation. New grains are nucleated throughout the metal and grow; the heavily deformed high-dislocation-density cold-worked grains are replaced by new equiaxed low-dislocation-density grains. On prolonged heating at even higher temperatures, some of these grains grow at the expense of others, and a coarse-grained material (or even a single crystal) replaces the fine-grained recrystallised structure. The changes occurring during recrystallisation are readily apparent in the optical microscope, and are accompanied by drastic softening of the metal.

Macroscopic Defects in Metals

While vacancies, dislocations, etc. may be regarded as atomic defects, grains may be regarded as microscopic defects. There are also, however, what may conveniently be termed *macroscopic* defects in metals. Too often these are the result of poor design, poor processing or production, poor welding, careless handling or operating. Examples of these would be sharp re-entrant corners, crevices, casting defects, rolled-in mill-scale, rough-sheared edges, poorly machined surfaces, weld defects, surface scratches, etc. However, by far the most important macroscopic defect, which is inherent in the uses to which metals are put, and the ways in which they are formed, is the presence of stresses, and particularly tensile stresses. These stresses may be either applied, resulting from the fact that the metal is being used in a load-bearing capacity, or residual. Residual stresses may either be microstresses arising, for example, from dislocations piled up against a grain boundary or, much more importantly, macrostresses. Residual macrostresses arise from a very wide range of effects, e.g. forming, heat treating, machining, welding and assembling operations can all give rise to high residual tensile stresses over relatively large regions.

Structure of Metal Surfaces and Surface Defects

So far the structure of pure metals has been discussed with reference to bulk characteristics and continuous crystals. However, corrosion is essentially a surface phenomenon and it is necessary to consider how the structure and defects already described interact with free surfaces. At this stage it is convenient to consider only a film-free metal surface, although of course in most corrosion phenomena the presence of surface films is of the utmost importance. Furthermore, it is at free surfaces that the hard sphere model of metals

first begins to become inadequate, particularly when surface films are considered, or in aqueous environments, when an electrical double layer exists.

Figure 20.36a shows schematically a smooth metal surface, although it should always be borne in mind that even a high-quality electropolished surface will not be flat but will have a roughness of about 5 nm or so high, while the roughness on a high-quality machined surface may be about 1 μm or so high. In most real materials there will be grain boundaries meeting the surface as shown in Fig. 20.36a. Furthermore, it is extremely unlikely that the plane of the metal surface will coincide with a low-index low-energy high-atomic-density close-packed plane, as in grain *B*. In most cases the plane of the metal surface will be a high-index high-energy low-atomic-density plane, as in grains *A* and *C*.

On an atomic scale, metal surfaces are usually described in terms of the terrace-ledge-kink model shown in Fig. 20.36b. Essentially, it is suggested that clean metal surfaces consist of low-energy low-index terraces separated by ledges of monatomic height which occasionally contain monatomic kinks.

By their nature, dislocations cannot end suddenly in the interior of a crystal; a dislocation line can only end at a free surface or a grain boundary (or form a closed loop). Where a screw dislocation intersects a free surface there is inevitably a step or ledge in the surface, one atomic layer high, as shown in Fig. 20.30c. Furthermore, the step need not necessarily be straight and will, in fact, almost certainly contain kinks.

The co-ordination number of an atom lying in a (111) surface of an f.c.c.

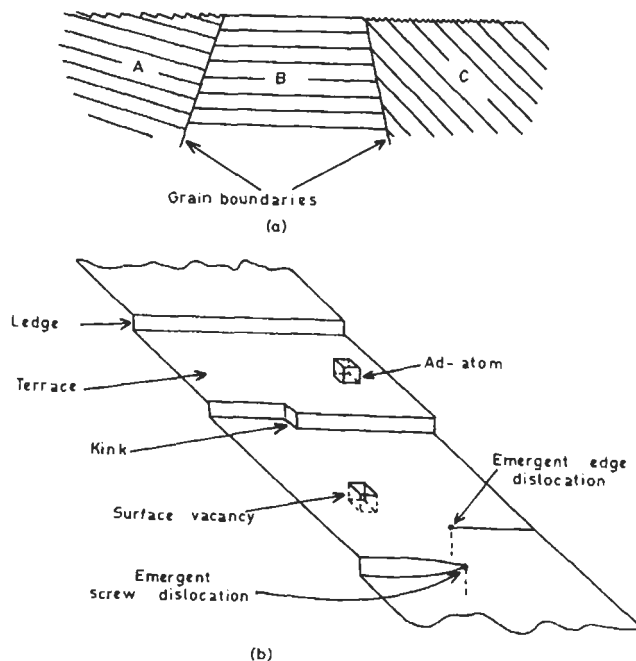


Fig. 20.36 (a) Grains of different orientation intersecting a free surface and (b) the terrace-ledge-kink model of a free metal surface

crystal is 9, compared with the bulk value of 12; an atom at a step in the surface has a co-ordination number of 7 while that of an atom at a kink in a step is only 6. The latter atom, therefore, is least strongly bound to the metal crystal and is likely to be the first to be removed from the lattice in any active dissolution process. Clearly, however, this removal does not eliminate the kink and, in fact, it is impossible, by repeated removal of atoms, to eliminate the step caused by a screw dislocation intersecting a free surface. There are, however, in addition to screw dislocations, many other causes of steps or ledges on metal surfaces, for example low-index planes intersecting the surface at an acute angle (see grain *A* in Fig. 20.36*a*).

As shown in Fig. 20.36*b*, an edge dislocation intersecting a free surface does not cause a step. However, the atoms adjacent to the core of the dislocation, being in non-equilibrium positions, have a higher energy than other atoms in the surface. The emergent ends of both edge and screw dislocations thus represent potential sites for preferential dissolution. Finally, there may be vacancies in the surface and ad-atoms on the surface (Fig. 20.36*b*).

Structure of Alloys

The discussion so far has been limited to the structure of pure metals, and to the defects which exist in crystals comprised of atoms of one element only. In fact, of course, pure metals are comparatively rare and all commercial materials contain impurities and, in many cases also, deliberate alloying additions. In the production of commercially pure metals and of alloys, impurities are inevitably introduced into the metal, e.g. manganese, silicon and phosphorus in mild steel, and iron and silicon in aluminium alloys. However, most commercial materials are not even nominally pure metals but are alloys in which deliberate additions of one or more elements have been made, usually to improve some property of the metal; examples are the addition of carbon or nickel and chromium to iron to give, respectively, carbon and stainless steels and the addition of copper to aluminium to give a high-strength age-hardenable alloy.

Components and Phases

Impure metals and alloys exhibit all the structural features and crystal defects of the pure metals already discussed. In addition, however, impure metals and alloys exhibit many structures which are not observed in pure metals, and which, in many instances, have an extremely important effect on the properties, particularly the corrosion resistance. However, before dealing with the structure of impure metals and alloys, it is necessary to consider the concept of metallurgical components, phases, constituents and equilibrium phase diagrams.

The fundamental difference between pure metals and impure metals and alloys arises from the fact that there is only one atomic species present in the former, while there are two or more present in the latter; thus a pure metal is a single-component system, a pure binary alloy is a two-component system, while impure metals and alloys, strictly speaking, are multi-component

systems. It is, however, usually valid to neglect the impurities and, for example, to consider a commercial brass as a binary Cu-Zn alloy, i.e. as a two-component system.

Gibbs' phase rule, as applied to metallurgical systems (i.e. under conditions of constant pressure) indicates that pure metals, being single-component systems, can only co-exist as two phases in equilibrium at a single temperature. Thus pure copper, for example, exhibits three phases, namely solid f.c.c. copper, liquid copper and gaseous copper. Any two of these phases, say solid and liquid copper, can co-exist in equilibrium at only one temperature, i.e. the melting point of copper. Pure iron exhibits four phases, namely two solid phases (f.c.c. and b.c.c. iron (see Table 20.5)) and a liquid and a gaseous phase. Alloys, on the other hand, being multi-component systems, can exhibit two or more phases in equilibrium over a range of temperatures. The phases which are present in an alloy, and their composition and distribution, markedly affect many of the properties of the alloy, including corrosion resistance.

Solid Solutions

When a pure metal *A* is alloyed with a small amount of element *B*, the result is ideally a homogeneous random mixture of the two atomic species *A* and *B*, which is known as a solid solution of *B* in *A*. The solute *B* atoms may take up either interstitial or substitutional positions with respect to the solvent atoms *A*, as illustrated in Figs. 20.37*a* and *b*, respectively. Interstitial solid solutions are only formed with solute atoms that are much smaller than the solvent atoms, as is obvious from Fig. 20.37*a*; for the purpose of this section only three interstitial solid solutions are of importance, i.e. Fe-C, Fe-N and Fe-H. On the other hand, the solid solutions formed between two metals, as for example in Cu-Ag and Cu-Ni alloys, are always substitutional (Fig. 20.37*b*). Occasionally, substitutional solid solutions are formed in which the

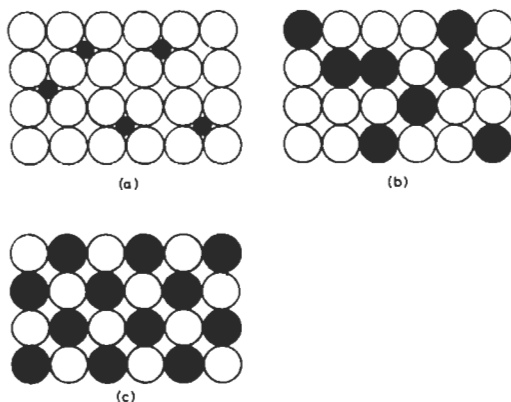


Fig. 20.37 (a) Interstitial solid solution, (b) random substitutional solution and (c) an ordered substitutional solid solution forming a superlattice

distribution of B in A is not random (Fig. 20.37c) and such solid solutions are said to be *ordered*, and to exhibit a *superlattice*. Order-disorder transitions are observed with temperature changes. Superlattices are observed in the Cu-Au, Cu-Zn and Fe-Ni systems.

There are a number of differences between interstitial and substitutional solid solutions, one of the most important of which is the mechanism by which diffusion occurs. In substitutional solid solutions diffusion occurs by the vacancy mechanism already discussed. Since the vacancy concentration and the frequency of vacancy jumps are very low at ambient temperatures, diffusion in substitutional solid solutions is usually negligible at room temperature and only becomes appreciable at temperatures above about $0.5T_M$ where T_M is the melting point of the solvent metal (K). In interstitial solid solutions, however, diffusion of the solute atoms occurs by jumps between adjacent interstitial positions. This is a much lower energy process which does not involve vacancies and it therefore occurs at much lower temperatures. Thus hydrogen is mobile in steel at room temperature, while carbon diffuses quite rapidly in steel at temperatures above about 370 K.

Segregation at Dislocations and Grain Boundaries

In practice, the distribution of solute atoms in a solid solution is not ideally homogeneous. There is almost invariably a stress field around any solute atom in solid solution, and there is therefore a tendency for these atoms to migrate to regions of the crystal lattice that are already strained, in particular to grain boundaries and to dislocations. Thus in impure metals and alloys there is an inherent tendency for impurities and alloying additions to segregate at grain boundaries and around the cores of dislocations. Segregation of carbon and nitrogen to dislocations in steels has a very significant effect on their mechanical properties, and in particular is responsible for their sharp yield point; similar segregation may also (see Section 1.3) affect the corrosion behaviour of cold-worked steels. The segregation of impurities and alloying elements to grain boundaries is clearly of relevance in any consideration of the strength and reactivity of grain boundaries and, in particular, of intergranular corrosion, temper embrittlement, etc.

In addition, it has fairly recently been recognised that impurities and alloying elements will also tend to segregate to free surfaces. The implications of this for corrosion resistance and particularly for passive-film formation have received relatively little attention.

Limited and Complete Solid Solubility

Just as the saturated solubility of sugar in water is limited, so the solid solubility of element B in metal A may also be limited, or may even be so low as to be negligible, as for example with lead in iron or carbon in aluminium. There is extensive interstitial solid solubility only when the solvent metal is a transition element and when the diameter of the solute atoms is < 0.6 of the diameter of the solvent atom. The Hume-Rothery rules state that there is extensive substitutional solid solubility of B in A only if:

- (a) The atomic diameters of *A* and *B* do not differ by more than 15%.
- (b) The two elements have similar electronegativity. (Note: electronegativity is the power of an element to attract electrons to itself when present in a molecule or in an aggregate of unlike atoms; it is a different property from the electrode potential, which depends on the free energy difference between an element in its standard state and a compound or ion in solution (see Section 20.1).) In addition a metal of a lower valency tends to dissolve a metal of a higher valency more readily than vice versa.

However, just as two liquids may be completely miscible and form a complete range of solutions from one pure liquid to the other, so certain metals, for example copper and nickel, exhibit complete solid solubility over the whole range of compositions from pure copper to pure nickel. Clearly for two metals to be soluble in each other over the whole compositional range, they must have the same crystal structure, i.e. they must be isomorphous.

Intermediate Phases and Intermetallic Compounds

When metal *A* is alloyed with enough element *B* to exceed the solid solubility of *B* in *A*, a new phase is formed. This may be the other terminal solid solution of *A* in *B*. Alternatively, an intermediate solid-solution phase, with a crystal structure different from that of either of the terminal solid solutions, may be formed over a range of compositions. An example of this is the so-called β -phase in brasses which is the stable phase at room temperature over the composition range 47–50% Zn. In some alloys, intermediate phases are formed that are best regarded as compounds. Examples are Fe_3C (cementite) in the Fe–C system and the intermetallic compounds MgNi_2 and Mg_2Ni formed in the Mg–Ni system. Whereas solid solutions are stable over a range of compositions, compounds have a unique composition; cementite, for example, corresponds to Fe–25at.% C (Fe–6.7wt.% C).

Equilibrium Phase Diagrams

In alloys, as in pure metals, the stable phase or phases change with changing temperature. Furthermore, in alloys the stable phase or phases, and the composition of these phases, changes with the composition of the alloys. These changes are best represented by equilibrium phase diagrams. These define the stability and composition of the phases that can occur in an alloy system as a function of temperature and alloy composition, under conditions of constant pressure. Phase diagrams are in many ways analogous to Pourbaix diagrams, which define the stability of phases in a metal/water system as a function of potential and pH, and like *E*–pH diagrams, phase diagrams have certain limitations. Firstly it must be emphasised that they are equilibrium phase diagrams, and that they only predict the stability and composition of phases under equilibrium conditions. They give no indication of how rapidly equilibrium will be achieved in practice, nor do they give any indication of the distribution of the phases at equilibrium. Somewhat analogously, *E*–pH

diagrams give no information as to the rate at which a particular metal will corrode, or as to the protectiveness of a particular passive film. Secondly, equilibrium phase diagrams give no information whatsoever as to the existence of metastable phases, some of which are of the utmost practical significance. These limitations become particularly important under conditions of rapid temperature change. Phase diagrams, in contrast to E -pH diagrams, are always determined experimentally, although they can be explained and to a certain extent qualitatively predicted from thermodynamic data and considerations. Nevertheless, in spite of these limitations, phase diagrams are an extremely important and useful metallurgical tool. (See also Section 1.4.)

Binary Isomorphous Phase Diagrams

Although ternary and quaternary phase diagrams are beyond the scope of this section, it is appropriate to deal with the various types of binary phase diagram by referring to some specific alloys. The simplest phase diagram refers to an isomorphous alloy system in which there is complete solid solubility. By way of example, the Cu-Ni phase diagram is shown in Fig. 20.38. This phase diagram indicates that at 1600K an alloy containing 70% Cu is a liquid (point a in Fig. 20.38). On slow cooling, this alloy starts to solidify when the liquidus line is reached, i.e. point b at about 1500K. At this point grains of a solid solution containing about 53% Cu are nucleated from the liquid containing 70% Cu, and start to grow. As the temperature continues to fall, the composition of the liquid follows the liquidus line while that of the solid falls along the solidus line, until at 1470K the alloy consists of a mixture of a solid solution containing 62% Cu and a liquid containing

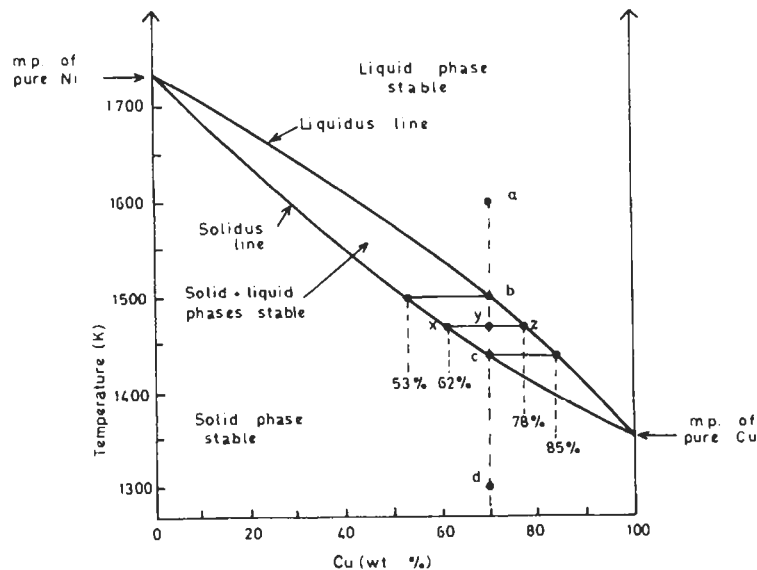


Fig. 20.38 Nickel-copper phase diagram

78% Cu (Fig. 20.38). Furthermore, the fraction of solid in the two-phase mixture is given by the ratio of the lengths yz/xz , while the fraction of liquid is given by xy/xz . This is known as the *lever rule*. On further slow cooling the solidus line is reached, i.e. point *c* at about 1430K, when solidification of the alloy is complete; the last liquid to freeze contains about 85% Cu, while the last solid to solidify contains 70% Cu. At 1300K, for example, and indeed at all temperatures below the solidus, an alloy containing 70% Cu is a solid (point *d* in Fig. 20.38). Clearly the phase change in this transformation is liquid \rightarrow solid. The microstructure of a homogeneous single-phase solid-solution alloy is indistinguishable from that of a pure metal, as shown in Fig. 20.28 (bottom).

Coring

If the alloy is cooled sufficiently slowly, the alloy itself and all the grains in it will be homogeneous after solidification. If, on the other hand, the alloy is cooled rather more rapidly, the grains will not be homogeneous but will be cored. During cooling, the composition changes in the solid phase involve solid state diffusion; if the temperature falls too rapidly, therefore, there is insufficient time for diffusion. In the Cu-30Ni alloy referred to earlier, clearly the centre of the grains, the first metal to have solidified, would be nickel rich (i.e. low in copper) while the grain boundary regions, the last metal to have solidified, would be copper rich. Coring is eliminated by annealing at high temperatures to permit diffusion and homogenisation to take place.

Eutectic Phase Diagrams

The equilibrium phase diagram for Pb-Sb alloys represents a simple eutectic system and is shown in Fig. 20.39. This type of phase diagram is often observed when there is negligible solid solubility of the two metals in each other and no intermediate phases are formed. The point *E* is the eutectic point, T_E the eutectic temperature and C_E the eutectic composition, in this case approximately 520K and 13% Sb, respectively. Like a pure metal, an alloy of eutectic composition freezes at a single temperature T_E , instead of over a temperature range, as in the case of the Cu-30Ni alloy already discussed. Unlike a pure metal, however, a eutectic alloy freezes to give a mixture of two phases, in this case Pb and Sb; in general terms, therefore, a eutectic reaction involves liquid \rightarrow solid α + solid β .

A hyper-eutectic alloy containing, say, 50% Sb starts to freeze when the temperature reaches the liquidus line (point *a* in Fig. 20.39). At this temperature pure pro-eutectic Sb nucleates; as the temperature continues to fall, more antimony is deposited from the melt, and the composition of the liquid phase moves down the liquidus line to the eutectic point. When this is reached, the remainder of the melt solidifies. The microstructure of alloys of eutectic composition varies somewhat with alloy system, but generally consists of an aggregate of small particles, often platelets, of one of the phases comprising the eutectic in a continuous matrix of the other phase. Finally, the microstructure of the hypereutectic 50% Sb alloy already mentioned

consists of primary (pro-eutectic) antimony surrounded by the eutectic constituent, as illustrated in Fig. 20.40. This microstructure is clearly to be expected from the solidification sequence just described.

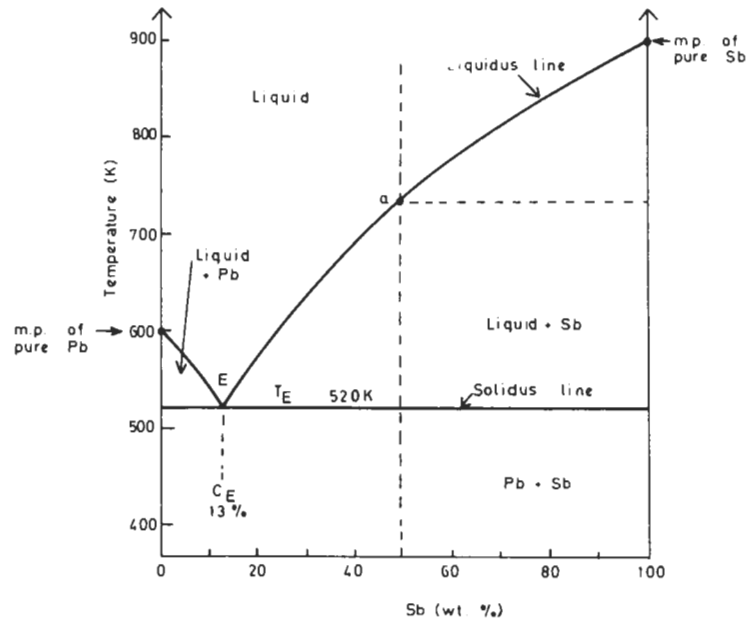


Fig. 20.39 Lead-antimony phase diagram

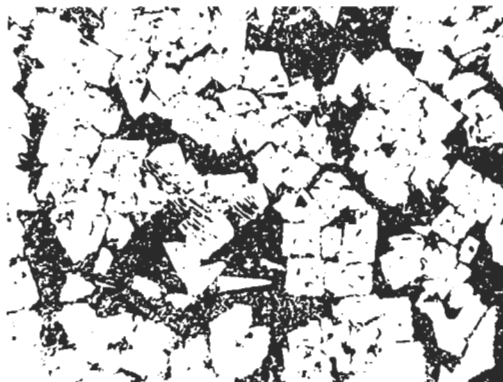


Fig. 20.40 Light micrograph showing the microstructure of a hyper-eutectic Pb-50Sb alloy ($\times 50$)

More Complex Binary Phase Diagrams

Most phase diagrams, however, are more complex than those shown in Figs 20.38 and 20.39. Thus in most eutectic systems there is some appreciable

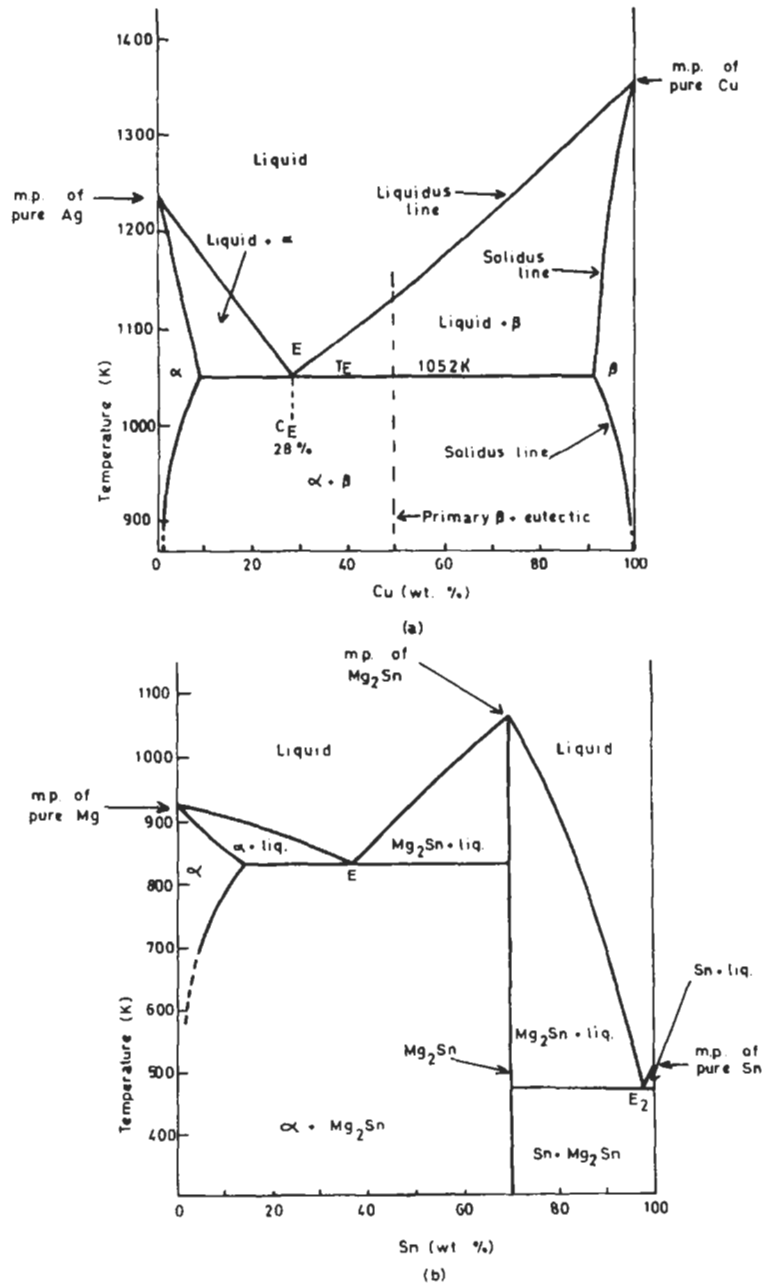


Fig. 20.41 (a) Silver-copper phase diagram and (b) magnesium-tin phase diagram

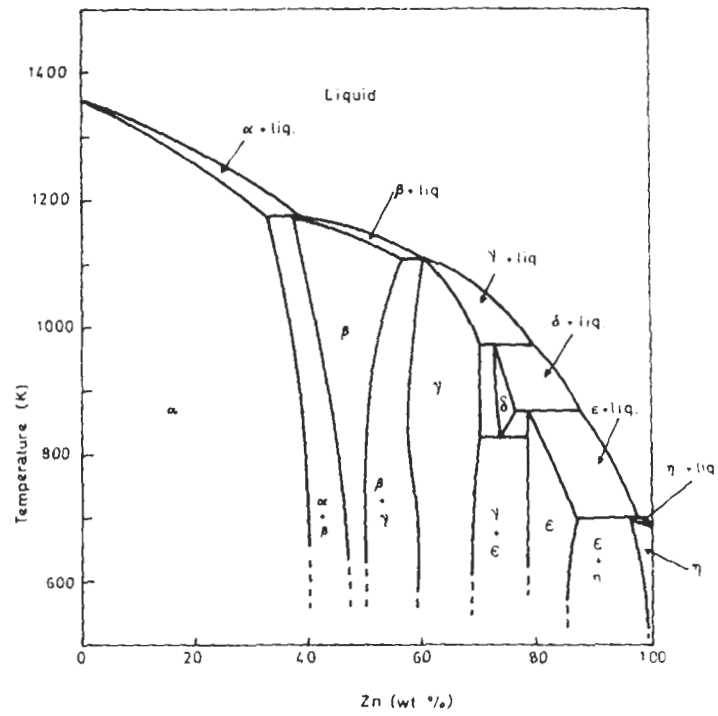


Fig. 20.42 Copper-zinc phase diagram

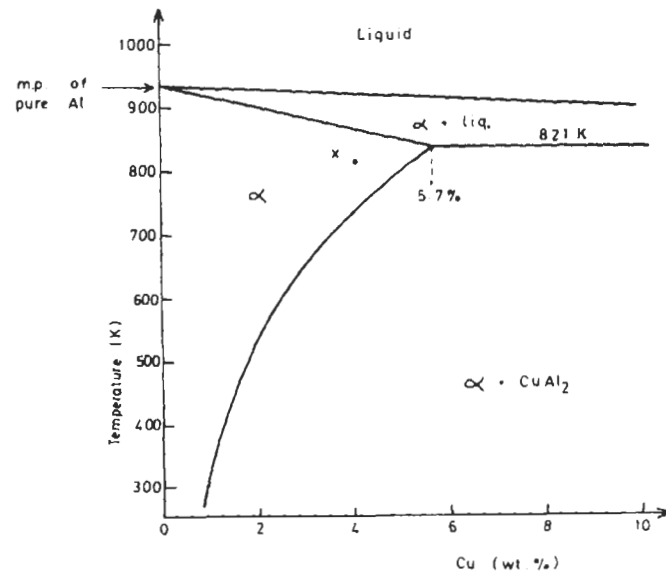


Fig. 20.43 Aluminium-rich end of the aluminium-copper phase diagram

solid solubility, as in the Ag-Cu phase diagram shown in Fig. 20.41a. At ambient temperatures, therefore, an Ag-50Cu alloy would contain two components (Ag and Cu), two phases (the α and β solid solutions) and two constituents (primary pro-eutectic β and the eutectic mixture of $\alpha + \beta$). Furthermore, in many alloy systems intermediate phases and/or intermetallic compounds are formed. Figure 20.41b, for example, illustrates the Mg-Sn phase diagram; this exhibits two eutectic reactions and the intermetallic compound Mg_2Sn . Finally, a number of other reactions, in addition to the eutectic reaction, are observed; of particular importance are (on cooling in all cases):

1. The *eutectoid* reaction: solid $\alpha \rightarrow$ solid $\beta +$ solid γ .
2. The *peritectic* reaction: liquid + solid $\alpha \rightarrow$ solid β .
3. The *peritectoid* reaction: solid $\alpha +$ solid $\beta \rightarrow$ solid γ .

By way of example, the Cu-Zn phase diagram shown in Fig. 20.42 exhibits a number of different intermediate phases (β , γ , δ , etc.) and a number of peritectic reactions and a eutectoid reaction. In many instances it is not necessary to consider a complete phase diagram. Thus Fig. 20.43 illustrates the Al-rich end of the Al-Cu phase diagram and is used below in a discussion

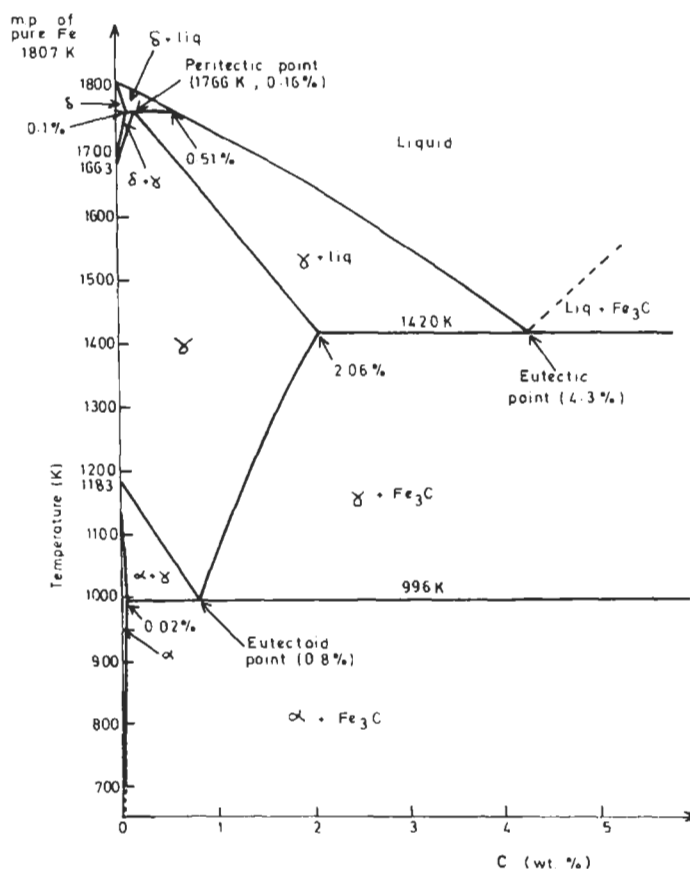


Fig. 20.44 Iron-rich end of the metastable Fe-Fe₃C phase diagram

of precipitation hardening. Again, Fig. 20.44 shows the Fe-Fe₃C phase diagram, the great practical importance of which is in no way reduced by the fact that one of the components in it, namely Fe₃C (cementite), is a metastable compound. The true equilibrium diagram, in which graphite appears in place of cementite, is of use only when cast irons are being considered, as opposed to steels. Other phase diagrams which are of particular significance are the iron-rich ends of the Fe-Ni and Fe-Cr systems, which are shown in

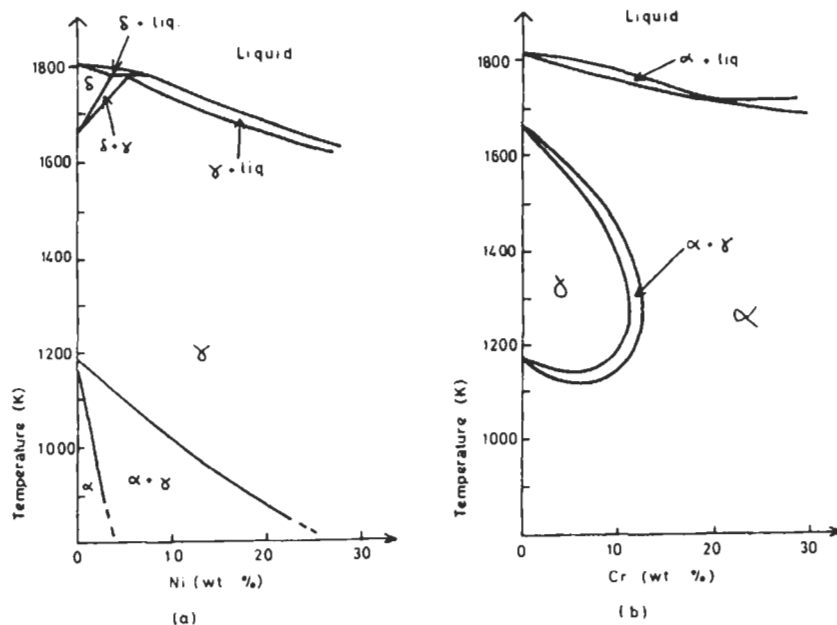


Fig. 20.45 (a) Iron-rich end of the iron-nickel phase diagram and (b) iron-rich end of the iron-chromium phase diagram

Figs. 20.45a and b, respectively. It follows from the diagrams that Ni and C are austenite (γ -phase) stabilisers while Cr is a ferrite (α -phase) stabiliser. The fact that the interstices in an f.c.c. structure are bigger than those in a b.c.c. structure accounts for the fact that C is much more soluble in f.c.c. iron (austenite) than in b.c.c. iron (ferrite) (Fig. 20.44).

The Fe-Fe₃C Phase Diagram

Because of the great practical importance of steels it is necessary to discuss the Fe-C system in rather more detail. The Fe-Fe₃C phase diagram consists of the following three reactions

1. At 1766K and 0.16% C the peritectic reaction: liquid Fe + δ - Fe (b.c.c.) \rightarrow γ - Fe (f.c.c.).
2. At 1420K and 4.3% C the eutectic reaction: liquid Fe \rightarrow γ - Fe (f.c.c.) + Fe₃C.
3. At 996K and 0.80% C the eutectoid reaction: γ - Fe (f.c.c.) \rightarrow α - Fe (b.c.c.) + Fe₃C.

The peritectic transformation generally has little effect on the structure, properties or corrosion resistance of steels at room temperature; an exception to this occurs in the welding of certain steels, when δ -ferrite can be retained at room temperature and can affect corrosion resistance. Furthermore, since most steels contain less than about 1.0% C (and by far the greatest tonnage contains less than about 0.3% C) the eutectic reaction is of relevance only in relation to the structure and properties of cast irons, which generally contain 2–4% C. This discussion, therefore, will be limited to the eutectoid reaction that occurs when homogeneous austenite is cooled.

Decomposition of Austenite

When austenite is cooled, the structures which result from the eutectoid reaction depend on the temperature at which the transformation takes place. In practice, of course, steels are generally continuously cooled at a rate which may vary from very rapid (quenching) to very slow (furnace cooling). However, it is useful and valid to simplify the situation by assuming that the transformation occurs isothermally. In other words, therefore, we shall consider initially the reactions which occur when a steel containing 0.8% C (i.e. of eutectoid composition) is very rapidly quenched from, say, 1400K to some temperature $T < 996\text{K}$, at which decomposition of the austenite takes place. In general, the structures produced on slow continuous cooling approximate to those resulting from high-temperature isothermal transformation, while rapid continuous cooling results in structures which approximate to those obtained by intermediate-temperature isothermal transformation.

Formation of Pearlite

If austenite is allowed to transform just below 996K, the reaction product, as predicted by the Fe-Fe₃C phase diagram, is the α - Fe + Fe₃C eutectoid. This eutectoid constituent is known as *pearlite*, and consists of alternate platelets of ferrite (α -Fe) and cementite (Fe₃C), the former being the continuous phase. The decomposition of austenite to pearlite involves nucleation of pearlite, which occurs almost exclusively at austenite grain boundaries, followed by growth of pearlite; both processes involve the solid-state diffusion of carbon in iron. Immediately after quenching, therefore, the structure of the steel consists of untransformed austenite, as shown schematically in Fig. 20.45a. At some later time, nucleation of a number of colonies of pearlite will have occurred at the austenite grain boundaries, as shown in Fig. 20.45b; at this stage about 10% of the austenite has transformed. At some later time still, growth of the pearlite will have occurred by nucleation of new α -Fe and Fe₃C platelets and by extensive edge-wise growth of existing platelets as shown in Fig. 20.45c; at this stage about 90% of the austenite has transformed and eventually transformation will be complete.

In fundamental terms, the transformation temperature affects both the driving force for the decomposition of austenite and the diffusion rate of carbon. In effect, therefore, the transformation temperature alters both the rate of nucleation and the rate of growth. This in turn manifests itself in

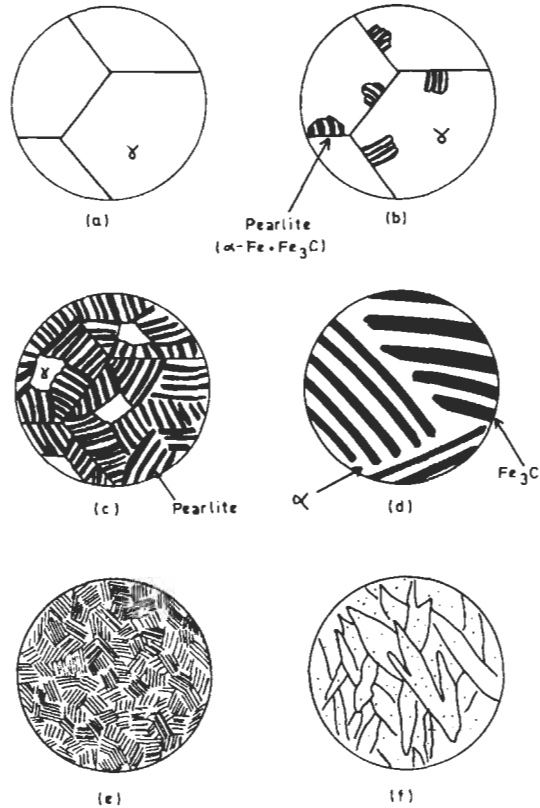


Fig. 20.46 Some of the pearlitic and bainitic microstructures observed in eutectoid steels after various heat treatments

different transformation times at different temperatures. Furthermore, the spacing of the pearlite platelets is characteristic of the temperature at which transformation occurred, the lower the transformation temperature the finer are the platelets, and the greater the hardness and the strength of the steel. The distinction between coarse and fine pearlite structures is shown in Fig. 20.46*d* and *e*, respectively; in practice the platelets in very fine pearlite may not be resolvable with a light microscope. The rate of transformation of carbon steels is also markedly affected by the presence of other alloying elements. However, a detailed consideration of the transformation and structure of low-alloy steels is beyond the scope of this section.

Formation of Bainite

At lower transformation temperatures (< 770K approx.) a second reaction, the formation of *bainite*, intervenes. Like pearlite, the bainite constituent in steels consists of a mixture of ferrite and an iron carbide and is formed by

a time-dependent nucleation and growth process involving diffusion of carbon. Bainite, however, grows as needlelike plates, which consist of very fine particles of carbide embedded in a ferrite matrix. The carbide particles can only be resolved in an electron microscope; in the light microscope only the acicular bainite needles are visible. The microstructure of a bainitic steel is shown schematically in Fig. 20.46f; the appearance of bainite, however, and the structure and composition of the carbides in it, vary somewhat with transformation temperature. Bainite is much harder than pearlite.

Formation of Martensite

Finally, at even lower transformation temperatures, a completely new reaction occurs. Austenite transforms to a new metastable phase called *martensite*, which is a supersaturated solid solution of carbon in iron and which has a body-centred tetragonal crystal structure. Furthermore, the mechanism of the transformation of austenite to martensite is fundamentally different from that of the formation of pearlite or bainite; in particular martensitic transformations do not involve diffusion and are accordingly said to be diffusionless. Martensite is formed from austenite by the slight rearrangement of iron atoms required to transform the f.c.c. crystal structure into the body-centred tetragonal structure; the distances involved are considerably less than the interatomic distances. A further characteristic of the martensitic transformation is that it is predominantly athermal, as opposed to the isothermal transformation of austenite to pearlite or bainite. In other words, at a temperature midway between m_s , (the temperature at which martensite starts to form) and m_f , (the temperature at which martensite

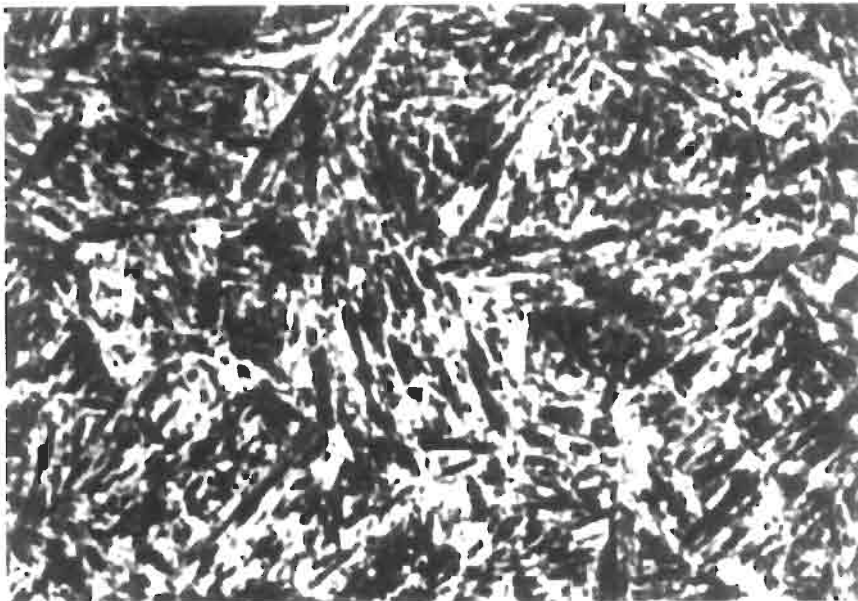


Fig. 20.47 Light micrograph showing the microstructure of a martensitic steel ($\times 550$)

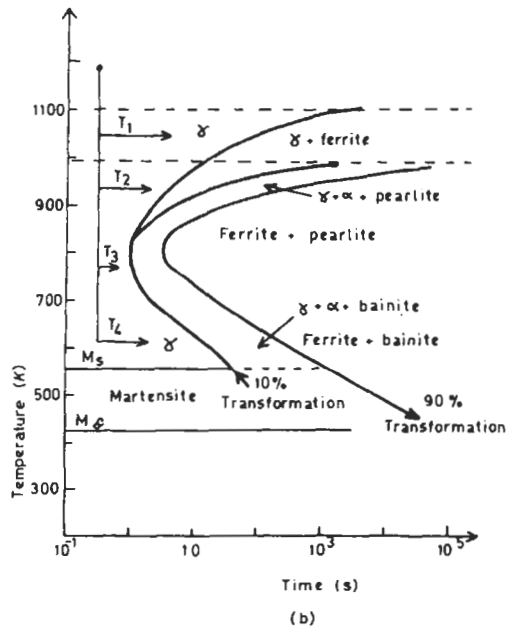
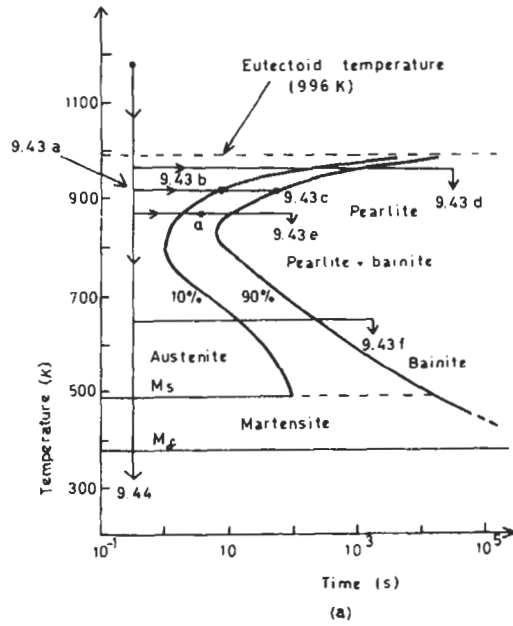


Fig. 20.48 Isothermal time temperature transformation curves for (a) a eutectoid steel and (b) a hypo-eutectoid steel

formation is apparently complete) the steel will consist of about 50% austenite and about 50% martensite; this transformation of 50% of the austenite to martensite is effectively instantaneous and no matter how long the steel is held at temperature, no further transformation will occur. Figure 20.47 illustrates the microstructure of a fully martensitic steel. The martensite platelets are heavily twinned, although this is only apparent in an electron microscope. In fact, in a eutectoid steel the m_f temperature is below room temperature although in a more common hypo-eutectoid steel containing about 0.2% C, $m_f \approx 720\text{K}$ and $m_s \approx 550\text{K}$. Other alloying elements also affect the temperature at which the martensite transformation takes place, and usually decrease it.

Isothermal Transformation Diagrams

Time-temperature-transformation (T-T-T) diagrams are used to present the structure of steels after isothermal transformation at different temperatures for varying times. The T-T-T diagram for a commercial eutectoid steel is shown in Fig. 20.48a. Also shown on the curves are the points at which the microstructures illustrated in Figs. 20.46 and 20.47 are observed, and the thermal treatments producing these structures. When a steel partially transformed to, say, pearlite, is quenched from point *a* in Fig. 20.48a to below m_f , the untransformed austenite transforms to martensite.

Transformation of Hypo-eutectoid Steels

As noted above, most steels are, in practice, hypo-eutectoid. Consider, by way of example, a low-alloy steel containing 0.3% C. The Fe-C phase diagram (Fig. 20.44) indicates that as a steel of this composition is cooled below about 1080K the equilibrium state is a two-phase structure containing primary, pro-eutectoid ferrite and austenite. On further cooling to below 996K the equilibrium structure consists of pro-eutectoid ferrite and pearlite. These differences are reflected in the rather more complicated T-T-T diagram used for this steel, shown in Fig. 20.48b.

Depending on the transformation temperature, the steel may transform to ferrite plus austenite (T_1 in Fig. 20.48b), to ferrite plus pearlite via ferrite plus austenite (T_2), directly to ferrite plus pearlite (T_3) or directly to ferrite plus bainite (T_4). The pro-eutectoid ferrite morphology, like the pearlite morphology, varies with the isothermal transformation temperature and also with the carbon content of the steel. The ferrite nucleates heterogeneously on austenite grain boundaries. Any pro-eutectoid ferrite in slightly hypo-eutectoid steels (about 0.6%) therefore tends to be distributed along the austenite grain boundaries, with the grain centres transforming later to pearlite, as shown schematically in Fig. 20.49a. At lower carbon contents, Widmanstätten pro-eutectoid ferrite is observed, as shown schematically in Fig. 20.49b, while in low-carbon steels massive ferrite is observed (Fig. 20.49c). It is important to re-emphasise that these pro-eutectoid ferrite structures also vary with isothermal transformation temperature and therefore, in practice, with cooling rate; they can also be altered by subsequent heat

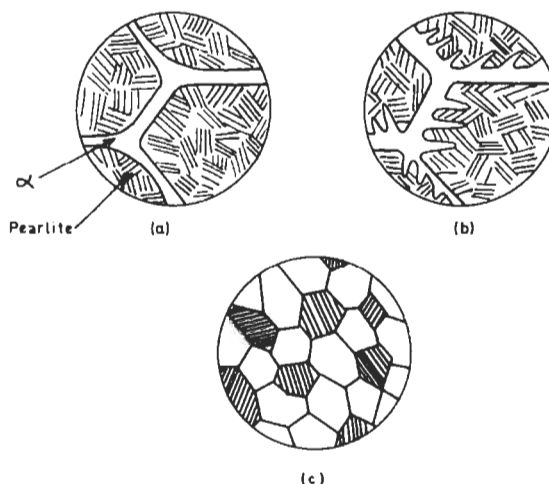


Fig. 20.49 Schematic illustration of some of the ferritic/pearlitic microstructures observed in hypo-eutectoid steels after various heat treatments

treatment and working. Grain-boundary and Widmanstätten ferrite are generally undesirable and result in poor mechanical properties. Figure 20.49, incidentally, illustrates some of the more important structures observed in two-phase alloys generally.

The higher the carbon content of a hypo-eutectoid steel, the more pearlite there will be in a ferritic/pearlitic structure and the greater will be the strength of the steel, other factors (grain-size, pearlite spacing, etc.) being equal.

Tempering of Martensite

As-quenched martensite is extremely hard, but also extremely brittle. The hardness of as-quenched martensite, which also increases with increasing carbon content, is due partly to the strain involved in retaining the carbon in solid solution in body-centred tetragonal iron, and partly, in low-carbon martensites, to their very high dislocation density. The martensite reaction in steels is not reversible and on reheating as-quenched martensite (Fig. 20.50a) to various temperatures below 996K, the carbon tends to precipitate out of solid solution; this process is known as *tempering*. On tempering at about 370–520K the carbon precipitates out as the so-called ϵ -carbide, which may be written as $\text{Fe}_{2.4}\text{C}$ and has a different structure from cementite. These carbides precipitate on certain crystallographic planes and on the twin boundaries in the martensite plates, forming what is known as a *Widmanstätten* structure, as shown schematically in Fig. 20.50b. on tempering at 520–770K, cementite particles are precipitated on twin boundaries and on boundaries between martensite platelets, leaving a matrix of ferrite as shown in Fig. 20.50c. Eventually the cementite particles grow and become spheroidal in shape, while the twinned structure breaks down, and fine equiaxed ferrite

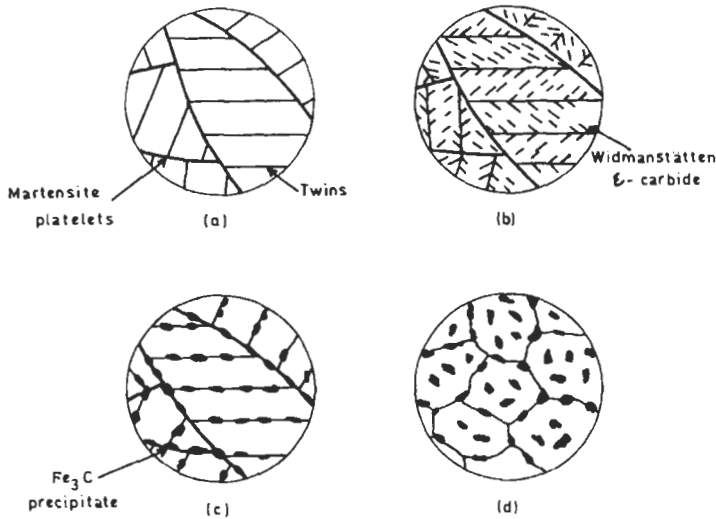


Fig. 20.50 Some of the microstructures observed during the tempering of martensite

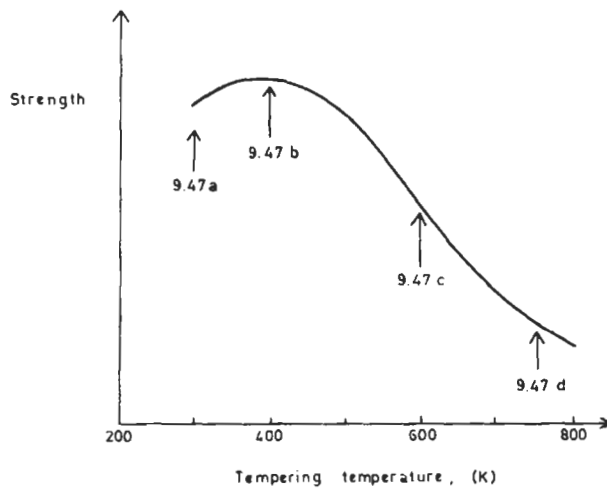


Fig. 20.51 Effect of tempering temperature on the strength and microstructure of martensite

grains are observed, as illustrated in Fig. 20.50d. On tempering, as the carbon precipitates out of solid solution, the strength and hardness of the steel falls progressively, as shown in Fig. 20.51, while the toughness increases. Quenched and tempered low-alloy steels are widely used where high-strength high-toughness materials are required.

Spheroidised Structures in Steels

On tempering or annealing martensite, bainite or even pearlite at even higher temperatures (about 970K) a structure consisting of coarse cementite spheroids (readily visible in a light microscope) in a ferrite matrix is obtained. This is the most stable of all ferrite/cementite aggregates, and it is also one of the softest.

The structures and phase transformations observed in steels have been dealt with in some detail not only because of the great practical importance of steels, but also because reactions similar to those occurring in steels are also observed in many other alloy systems. In particular, diffusionless transformations (austenite \rightarrow martensite), continuous precipitation (austenite \rightarrow pearlite) and discontinuous precipitation (austenite \rightarrow bainite and tempering of martensite) are fairly common in other alloy systems.

Strengthening Mechanisms in Metals

Many of the ways of increasing the strength of metals have already been dealt with in passing. For example, cold working a metal increases its dislocation density and therefore, as already discussed, increases its strength*. Substitutional solid solutions (e.g. austenitic stainless steels and brass) are normally stronger than the equivalent pure metals (i.e. iron and copper), as the lattice distortion involved hinders dislocation movement. This is known as *solid-solution hardening*. Metals with fine grain structures, produced by grain-refining treatments such as cold working followed by annealing to give recrystallisation, are stronger than coarse-grained materials and single crystals, since grain boundaries act as barriers to dislocation movement. Steels may be quenched and tempered to produce high-strength and high-toughness materials. Clearly, these all involve altering the structure of the metal in some way. A further very important strengthening mechanism, namely precipitation hardening, also involves microstructural changes.

Precipitation Hardening

Precipitation hardening (also called age hardening and dispersion hardening) is particularly important in high-strength aluminium alloys, but it is also used to strengthen other alloys, notably certain steels and nickel-base alloys. Consider, by way of example, the Al-Cu phase diagram shown in Fig. 20.43. At about 820K the equilibrium structure of an Al-4Cu alloy (point X in Fig. 20.43) is the single-phase α solid solution of copper in aluminium, as shown in Fig. 20.52a. On annealing at this temperature, i.e. on solution heat treating, this equilibrium state is readily achieved. At room temperature, since the limit of solid solubility decreases with decreasing temperature, the equilibrium structure consists of the α -solid solution plus the CuAl_2 intermetallic compound. This equilibrium state may be achieved by very slowly

* The processes involved in the nucleation and multiplication of dislocations during cold working are very complex, and beyond the scope of this section.

cooling the alloy from 820K to room temperature, and consists of very coarse discontinuous precipitates of CuAl_2 in an α matrix, as shown in Fig. 20.52*b*. However, on quenching the alloy to room temperature, diffusion (and therefore nucleation and growth of CuAl_2) is prevented, and the copper is retained in supersaturated solid solution, as shown in Fig. 20.52*c*. This super-saturated solid solution is relatively soft, weak and ductile. If this metastable supersaturated solid solution is then aged, i.e. heat treated at a relatively low temperature (370–520K), the excess copper again precipitates out of solid solution as CuAl_2 . In this case, however, the CuAl_2 particles are extremely fine, certainly sub-microscopic and under certain conditions only just resolvable in the electron microscope. The precipitation sequence varies

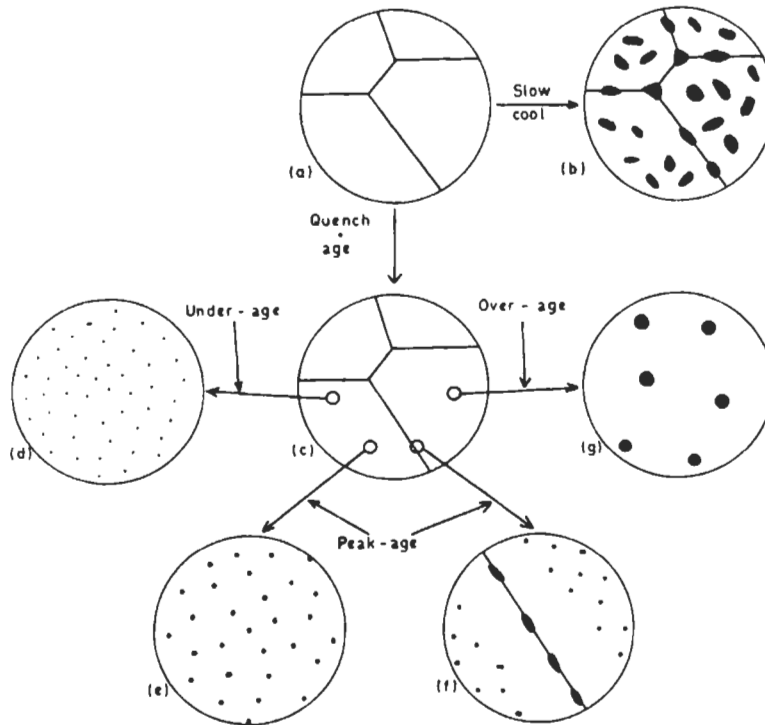


Fig. 20.52 Some of the microstructures observed during the heat treatment of precipitation-hardening aluminium alloys

from alloy to alloy but is generally quite complex and involves a number of intermediate metastable precipitates. The initial precipitates or coherent zones formed during the early stages of ageing (i.e. after relatively short times) interact with dislocations and tend to hinder their movement. This underaged condition is therefore stronger than the as-quenched condition, but, since the zones are extremely fine (Fig. 20.52*d*), and are readily sheared by moving dislocations (Fig. 20.53*a*), only moderately so. On further ageing, somewhat coarser, semi-coherent intermediate precipitates are formed (Fig. 20.52*e*). These interact strongly with dislocations and, since they are too

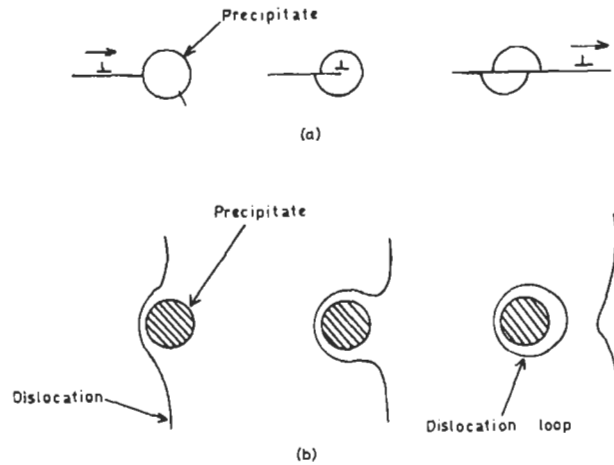


Fig. 20.53 (a) Dislocation shearing a precipitate particle and (b) a dislocation bowing round a precipitate particle

large to be sheared, form very effective barriers to dislocation motion. Dislocations can only move through the matrix by bowing round the precipitates and leaving behind dislocation loops, as shown in Fig. 20.53*b*, and in this peak-aged condition the alloy is strongest. If ageing is continued, a relatively coarse dispersion of the equilibrium precipitate is formed. In this overaged condition (Fig. 20.52*g*) the precipitates are too coarse and widely spaced to interact strongly with dislocation; they are relatively ineffective barriers to dislocation motion and the alloy therefore again has only intermediate strength. It should be emphasised, however, that even in the overaged condition the precipitates are still sub-microscopic.

The rate at which ageing occurs depends on the ageing temperature. At very low ageing temperatures, over-ageing is not observed in a realistic time

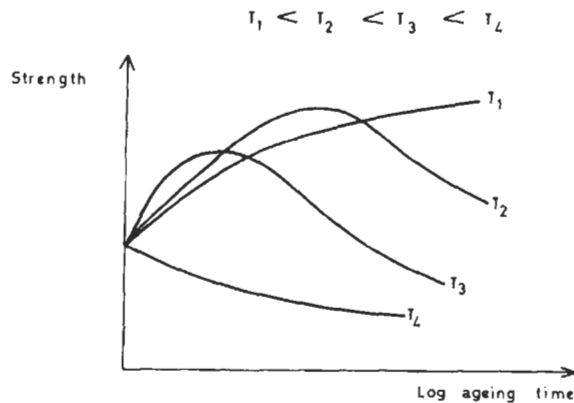


Fig. 20.54 Curves of strength against the logarithm of the ageing time for a precipitation-hardening aluminium alloy aged at different temperatures

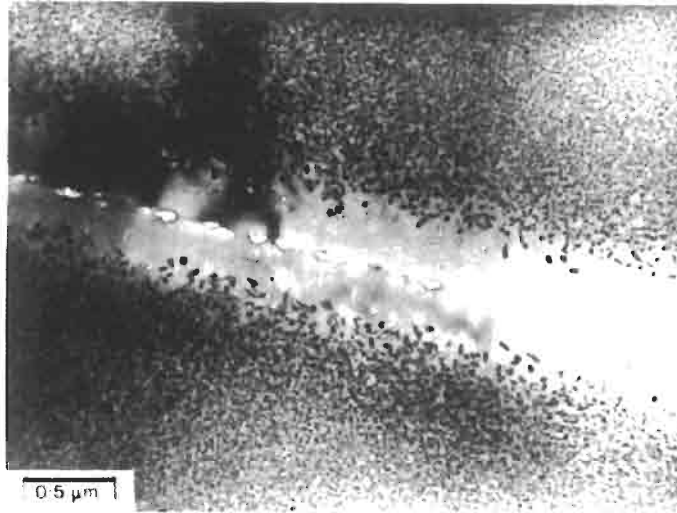


Fig. 20.55 Transmission electronmicrograph showing intergranular and intragranular precipitation and the precipitate-free zone adjacent to the grain boundary in a high-strength precipitation-hardening Al-Zn-Mg alloy ($\times 24\,000$, courtesy G. Lorimer)

scale while at high ageing temperatures the strength falls off almost immediately. In general, the lower the ageing temperature, the greater the peak hardness. These effects are illustrated schematically in Fig. 20.54.

During ageing, nucleation always occurs first at grain boundaries; the intergranular precipitates are therefore always coarser and more advanced than the intragranular precipitates. Furthermore, owing to vacancy and solute depletion, there is always a precipitate-free zone adjacent to the grain boundary. The grain-boundary structure of a peak-aged high-strength precipitation-hardening aluminium alloy is therefore as shown schematically in Fig. 20.52*f* and in the electronmicrograph in Fig. 20.55.

Complex Alloy Systems

Detailed consideration of the structure of many of the advanced and complex alloys which are of considerable technological importance (high-strength titanium alloys, nickel-base superalloys, etc.) is beyond the scope of this section, other than to point out that no new principles are involved. Certain titanium alloys, for example, exhibit a martensitic transformation, while many nickel-base superalloys are age hardening. Similarly, cast irons, although by no means advanced materials, are relatively complex; they are considered in Section 1.3 where *graphitisation* is discussed.

Inclusions in Metals

In conclusion, it must be emphasised again that commercial materials are never pure metals or pure binary or ternary alloys. They always contain

impurities which are not particularly beneficial to the properties of the material; however, so long as they are not positively detrimental (as in the case of carbon in certain austenitic stainless steels), their presence is tolerated as it would be uneconomic to remove them. Some of these impurities are in solid solution. Others, however, exist as inclusions which are quite unaffected by heat treatment, although they may be broken up by working. Examples are the Fe-Si-rich inclusions in aluminium alloys (Fig. 20.34), manganese sulphide inclusions in steel, etc. However, although these impurities may have a negligible effect on mechanical properties they can, in certain instances, markedly affect corrosion behaviour.

The concepts discussed in this section are dealt with in greater depth in References 1 to 10 inclusive, and specific examples of the effect of metallurgical structure on corrosion are considered in Section 1.3.

R. P. M. PROCTER

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21 USEFUL INFORMATION

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Table 21.1 Periodic Table

At. no.	Element	Symbol	At. wt.	Mass number of common isotopes	Periodic group	Valency - +	Density* ₁ at 20°C (g cm ⁻³)	Boiling* point (°C)
1	Hydrogen	H	1.0080	1, 2	1	1 1	0.07	-252.8
2	Helium	He	4.003	3, 4	0	Inert	0.147	-268.9
3	Lithium	Li	6.940	6, 7	1	1	0.534	1330
4	Beryllium	Be	9.013	9	2	2	1.848	2400, 2770
5	Boron	B	10.82	10, 11	3	3	2.34	2550
6	Carbon	C	12.011	12, 13	4	4 2, 4	3.52(D)	4830
7	Nitrogen	N	14.008	14, 15	5	3 1-5	0.808	-195.8
8	Oxygen	O	16.0000	16, 17, 18	6	2 6	1.14	-182.970
9	Fluorine	F	19.00	19	7	1 7	1.108	-188.2
10	Neon	Ne	20.183	20, 21, 22	0	Inert	1.204	-245.9
11	Sodium	Na	22.991	23	1	1	0.9712	883, 892
12	Magnesium	Mg	24.32	24, 25, 26	2	2	1.741	1107
13	Aluminium	Al	26.98	27	3	3	2.70	2400, 2450
14	Silicon	Si	28.09	28, 29, 30	4	4 4	2.33	2480, 3240
15	Phosphorus	P	30.975	31	5	3 3, 5	1.83(w)	280
16	Sulphur	S	32.066	32-34, 36	6	2 4, 6	2.07	444-600
17	Chlorine	Cl	35.457	35, 37	7	1 1, 5, 7	1.56	-34.7
18	Argon	Ar	39.944	36, 38, 40	0	Inert	1.40	-185.8
19	Potassium	K	39.100	39, 40, 41	1	1	0.86	760
20	Calcium	Ca	40.08	40, 42-44, 46, 48	2	2	1.55	1440
21	Scandium	Sc	44.96	45	3	3	2.50, 3.0*	2500, 2730
22	Titanium	Ti	47.90	46-50	4	3, 4	4.507	3260
23	Vanadium	V	50.95	51	5	2, 4, 5	5.96, 6.1*	3400
24	Chromium	Cr	52.01	50, 52-54	6	2, 6	7.19	2665
25	Manganese	Mn	54.94	55	7	2, 3, 4, 6, 7	7.42	2150
26	Iron	Fe	55.85	54, 56-58	8	2, 3	7.88	2900, 3000
27	Cobalt	Co	58.94	59	8	2, 3	8.85	2900
28	Nickel	Ni	58.71	58, 60-62, 64	8	2, 3	8.85	2820, 2730
29	Copper	Cu	63.54	63, 65	1	1, 2	8.95	2595
30	Zinc	Zn	65.38	64, 66-68, 70	2	2	7.133	906
31	Gallium	Ga	69.72	69, 71	3	3	5.91, 5.99*	2237
32	Germanium	Ge	72.60	70, 72-74, 76	4	4 4	5.36	2880, 2830
33	Arsenic	As	74.92	75	5	3 3, 5	5.73	613
34	Selenium	Se	78.96	74, 76-78, 80, 82	6	2 4, 6	4.81	685
35	Bromine	Br	79.916	79, 81	7	1 1, 5, 7	3.12	58.78
36	Krypton	Kr	83.80	78, 80, 82-84, 86	0	Inert	2.16	-152
37	Rubidium	Rb	85.48	85, 87	1	1	1.53	710, 679
38	Strontium	Sr	87.63	84, 86-88	2	2	2.60	1460, 1380
39	Yttrium	Y	88.91	89	3	3	5.51, 4.6*	3030
40	Zirconium	Zr	91.22	90-92, 94, 96	4	4	6.489	4400, 3580
41	Niobium	Nb	92.91	93	5	3, 5	8.57	5100, 4927
42	Molybdenum	Mo	95.95	92, 94-98, 100	6	3-5, 6	10.2	4600, 5560
43	Technetium	Tc	[99]	99a	7		11.46	
44	Ruthenium	Ru	101.1	96, 98-102, 104	8	3, 4, 6, 8	12.45	3900
45	Rhodium	Rh	102.91	103	8	3, 4	12.41	3900
46	Palladium	Pd	106.4	102, 104-106, 108, 110	8	2, 4	12.0	3200, 3980
47	Silver	Ag	107.880	107, 109	1	1, 2	10.5	2180, 2210
48	Cadmium	Cd	112.41	106, 108, 110-114, 116	2	2	8.65	765
49	Indium	In	114.82	113, 115	3	3	7.30	2000
50	Tin	Sn	118.70	112, 114-120, 122, 124	4	4 2, 4	7.31	2750, 2270
51	Antimony	Sb	121.76	121, 123	5	3 3, 5	6.62	1675, 1380

Notes. Isotopes: *n* - naturally radioactive isotopes, *a* - isotopes capable of being rendered artificially radioactive. Valency: principal valency is shown in bold type. Magnetic properties (at ordinary temperatures): *d* - diamagnetic, *p* - paramagnetic, *f* - ferromagnetic. Crystal-structure classification: 1 - c.p. hexagonal, 2 - f.c. cubic, 3 - b.c. cubic, 4 - diamond cubic, 5 - rhombohedral, 6 - orthorhombic, 7 - cubic, 8 - hexagonal, 9 - monoclinic, 10 - tetragonal.

At. no.	Melting* point (°C)	Work function (eV)	Ionisation potential (eV)		Mag. props.	Crystal struct.	Electron structure											
			I	II			$n = 1$	2	2	3	3	3	4	4	4	4	5	5
							$l = 0$	0	1	0	1	2	0	1	2	3	0	1
							1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p
1	-259.19		13.59		d	8	1											
2	-269.7		24.56	54.1	d	1	2											
3	180.54	2.4	5.4	75.7	p	3		1										
4	1277	3.9	9.32	18.2	d	1		2										
5	2030, 2300	4.6	8.28	25.1	d	6	He	2	1									
6	3727	4.4	11.27	24.8	d	4, 8	(2)	2	2									
7	-209.97		14.55	29.6	d	7, 8		2	3									
8	-218.8		13.62	35.2	p	5, 6, 7		2	4									
9	-219.6		17.43	34.9				2	5									
10	-248.67		21.56	40.9	d	2		2	6									
11	97.82	2.2	5.14	47.3	p	3				1								
12	650	3.6	7.64	15.0	p	1				2								
13	660.1, 659.7	4.0	5.97	18.8	p	2	Ne			2	1							
14	14.80	4.0	8.15	16.4	d	4	structure			2	2							
15	44.25		10.9	19.7	d	6, 7	(10)			2	3							
16	119.0	5.4	10.36	23.4	d	9, 6				2	4							
17	-101.0		12.90	23.7	d	10				2	5							
18	-189.4		15.76	27.5	d	2				2	6							
19	63.0	2.2	4.34	31.7	p	3							1					
20	850, 838	3.2	6.11	11.9	p	2							2					
21	1450, 1539	3.3	6.7	12.8		1						1	2					
22	1668	4.1	6.84	13.6	p	1, 3						2	2					
23	1900	4.1	6.71	14.1	p	3						3	2					
24	1875	4.6	6.74	16.7	p	1, 3						5	1					
25	1244	4.0	7.43	15.6	p	3, 7						5	2					
26	1539, 1536	4.4	7.83	16.5	f	2, 3	A			6	2							
27	1492, 1495	4.2	7.84	17.4	f	1, 2	structure			7	2							
28	1453	5.1	7.63	18.2	f	1, 2	(18)			8	2							
29	1083	4.4	7.72	20.2	d	2				10	1							
30	419.5	4.2	9.39	18.0	d	1				10	2							
31	29.8	4.1	5.97	20.5	d	6				10	2	1						
32	958, 937	4.8	8.13	16.0	d	4				10	2	2						
33	814	4.8	10.5	20.1	d	5				10	2	3						
34	217	4.7	9.73	21.5	d	8, 9				10	2	4						
35	-7.2		11.76	19.2	d	6				10	2	5						
36	-157.3		14.20	24.5	d	2				10	2	6						
37	38.9	2.2	4.17	27.3	p	3												1
38	768	2.4	5.69	11.0	p	2												2
39	1509	3.3	6.5	12.3	p	1, 2										1	2	
40	1852	4.0	6.95	14.0	p	1, 3										2	2	
41	2468	4.0	6.77		p	3										4	1	
42	2610	4.3	7.06		p	3										5	1	
43	2130	4.4	7.1													6	1	
44	2400, 2310	4.5	7.5	16.0	p	1				K						7	1	
45	1960	4.6	7.7	18.0	p	2				structure						8	1	
46	1552	4.9	8.1	19.8	p	2				(36)						10		
47	960.8, 960.880	4.6	7.58	21.4	d	2										10	1	
48	320.9	4.1	8.99	16.9	d	1										10	2	
49	156.2	4.0	5.79	18.9	d	10										10	2	1
50	231.9	4.3	7.30	14.6	d	4, 10										10	2	2
51	630.5	4.6	8.64	18.0	d	5										10	2	

*Values of densities, and of boiling and melting points, obtained from various sources do not always correspond.

†To convert density in g cm^{-3} to k gm^{-3} multiply by 10^3 .

For elements which are gases at 20°C and 1 atmosphere pressure the density of the liquid at the boiling point is given.

Table 21.1 (continued)

<i>At. no.</i>	<i>Element</i>	<i>Symbol</i>	<i>At. wt.</i>	<i>Mass number of common isotopes</i>	<i>Per- iodic group</i>	<i>Valency — +</i>	<i>Density* at 20°C (g cm⁻³)</i>	<i>Boiling* point (°C)</i>
52	Tellurium	Te	127.61	120, 122-6, 128, 130	6	2, 4, 6	6.24	990
53	Iodine	I	126.91	127	7	1, 5, 7	4.94	183
54	Xenon	Xe	131.30	124, 126, 128-32, 134, 136	0	Inert	3.52	112
55	Caesium	Cs	132.91	133	1	1	1.90	713, 690
56	Barium	Ba	137.36	130, 132, 134-8	2	2	3.5	1770, 1640
57	Lanthanum	La	138.92	138, 139	3	3	6.19	4200, 3470
58	Cerium	Ce	140.13	136, 138, 140, 142	3	3, 4	6.9	2900
59	Praseodymium	Pr	140.92	141	3	3, 4, 5	6.77	3026
60	Neodymium	Nd	144.27	142-6, 148, 150	3	3, 4	6.96	3180
61	Promethium	Pm	[147][145]	145a, 147a	3	3		
62	Samarium	Sm	150.35	144, 147, 148n, 149, 150, 152	3	2, 3	7.49	1600
63	Europium	Eu	152.0	151, 153	3	2, 3	5.24	
64	Gadolinium	Gd	157.26	152, 154-8, 160	3	3	7.95	2700
65	Terbium	Th	158.93	159	3	3, 4	8.33	2500
66	Dysprosium	Dy	162.51	158, 160-4	3	3	8.56	2300
67	Holmium	Ho	164.94	165	3	3	10.12, 8.8	2300
68	Erbium	Er	167.27	162, 164, 166-8, 170	3	3	9.16	2600
69	Thulium	Tm	168.94	169	3	3	9.35	2100
70	Ytterbium	Yb	173.04	168, 170-4, 176	3	2, 3	7.01	1500
71	Lutetium	Lu	174.99	175, 176n	3	3	9.85	1930
72	Hafnium	Hf	178.50	174, 176-80	4	4	13.09	5100, 5400
73	Tantalum	Ta	180.95	181	5	5	16.6	6000, 5425
74	Tungsten	W	183.86	180, 182-4, 186	6	4, 6	19.3	5400, 5930
75	Rhenium	Re	186.22	185, 187	7	1, 4, 7	21.04	5900
76	Osmium	Os	190.2	184, 186-90, 192	8	4, 6, 8	22.57	4600, 5500
77	Iridium	Ir	192.2	191, 193	8	3, 4, 6	22.65	4500
78	Platinum	Pt	195.09	192, 194-6, 198	8	2, 4	21.45	3800, 4530
79	Gold	Au	197.0	197	1	1, 3	19.32	2660, 2970
80	Mercury	Hg	200.61	196, 198-202, 204	2	1, 2	13.55	356.58
81	Thallium	Tl	204.39	203, 205, 206-8n, 210n	3	1, 3	11.85	1457
82	Lead	Pb	207.21	204, 206-8, 210-12n, 214	4	2, 4	11.36	1750, 1725
83	Bismuth	Bi	208.99	209, 210-12n, 214n	5	3, 5	9.80	1530, 1680
84	Polonium	Po	210	210-216n, 218n	6	2, 4	9.24	900, 965
85	Astatine	At	[210]	210n, 215n, 216n, 218n	7			
86	Radon	Rn	222	219n, 220n, 222n	0	Inert	4.40	-61.8
87	Francium	Fr	[223]	223n	1	1		
88	Radium	Ra	226.05	223-4n, 226n, 228n	2	2	5.0	1140
89	Actinium	Ac	227.05	227n, 228n	3	3		
90	Thorium	Tb	232	227-8n, 230-2n, 234n	3	3, 4	11.66	3800 ± 400
91	Protactinium	Pa	231	231n, 234n	3	3, 4, 5	15.4*	
92	Uranium	U	238.07	234n, 235n, 238n	3	3, 4, 5, 6	19.07	3818
93	Neptunium	Np	[237]	231a, 234a, 239a	3	3, 4, 5, 6		
94	Plutonium	PU	[242]	238n, 242n	3	3, 4, 5, 6	19 to 19.81	3235
95	Americium	Am	[243]	238-43a	3	2, 3, 4, 5	11.7	
96	Curium	Cm	[247]	238a, 240-3a	3	3		
97	Berkelium	Bk	[249]	244a, 245a	3	3, 4		
98	Californium	Cf	[251]	244a, 246a	3			
99	Einsteinium	Es	[254]		3			
100	Fermium	Fm	[253]		3			
101	Mendelevium	Md	[256]		3			
102	Nobelium	No	[254]		3			

*To convert density in g cm⁻³ to kg m⁻³ multiply by 10³.

At. no.	Melting* point (°C)	Work function (eV)	Ionisation potential (eV)		Mag. props.	Crystal struct.	Electron structure													
			I	II			$n = 4$	4	4	4	5	5	5	5	6	6	6	7		
							$l = 0$	1	2	3	0	1	2	3	0	1	2	0		
							4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7		
52	450	4.8	8.96	19.0	d	8	K	10		2	4									
53	113.7		10.44	19.0	d	6	structure	10		2	5									
54	-108		12.13	21.2	d	2	(36)	10		2	6									
55	28.7	1.9	3.89	23.4	d	3													1	
56	714	2.3	5.21	10.0	p	3													2	
57	920	3.3	5.61	11.4	p	8, 2, 3													2	
58	804, 785	2.8	6.54	12.3	p	8, 2, 3													2	
59	940	2.7	5.76		p	8, 3													2	
60	1024, 840	3.3	6.31		p	8, 3													2	
61																			2	
62	1052, 1350	3.2	5.6	11.4		5, 3													2	
63	1400		5.64	11.2	p	3													2	
64	1320		6.70		f	1													2	
65	1450		6.74			1	Xe	8	1	2										
66	1500		6.82		f	1	structure	9	1	2										
67	1500					1	(54)	10	1	2										
68	1525					1		11	1	2										
69	1600					1		12	1	2										
70	824		6.2	12.1		1, 2		13	1	2										
71	1700, 1652		5.0			1		14	1	2										
72	2000, 2222	3.6	5.5	14.8		1		14	2	2										
73	3000 ± 50	4.2	6.0		p	3		14	3	2										
74	3380, 3410	4.5	7.94		p	3		14	4	2										
75	3170	4.9	7.87	13.0		1		14	5	2										
76	2700	4.6	8.7	15.0	p	1		14	6	2										
77	2443	4.6	9.2	16.0	p	2		14	7	2										
78	1769	5.3	8.96	18.5	p	2		14	8	2										
79	1063.0	4.7	9.23	20.0	d	2		14	10	1										
80	-38.87, -38.36	4.5	10.44	18.8	d	5		14	10	2										
81	300	3.8	6.12	20.3	d	1, 3		14	10	2	1									
82	327.3, 327.425	4.0	7.42	15.0	d	2		14	10	2	2									
83	271.3	4.4	8.8	16.6	d	5		14	10	2	3									
84	254	4.6	8.2	19.0		9, 2		14	10	2	4									
85	approx. 302		9.6	18.0				14	10	2	5									
86	-71		10.75	20.0				14	10	2	6									
87	approx. 27	1.5		22																
88	700		5.27	10.1																
89	1050																			
90	1700, 1800	3.4			p	2														
91	approx. 1230	3.3			p															
92	1133	3.5	4.0			3, 10, 6	Rn		2											
93	637						structure		3											
94	640					9	(86)		4											
95									5											
96										6		1	2							
97										7		1	2							
98										8		1	2							
99										9		1	2							
100										10		1	2							
101										11		1	2							
102										12		1	2							
										13		1	2							

Table 21.2 Properties of some metals and alloys

	Thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$; 273–373 K)	Thermal expansion per kelvin (K^{-1})	Elect. resistivity ($\mu\Omega\text{m}$)*	Temp. coef. of res. per kelvin (in range 273–373 K) (K^{-1})	Mean specific heat in range 273–373 K ($\text{J kg}^{-1} \text{K}^{-1}$)	Young's modulus ($\text{MN m}^{-2}\dagger$ (or MPa))
Ag	418·400	$18\cdot9 \times 10^{-6}$	0·016	$4\cdot1 \times 10^{-3}$	225·936	$0\cdot07584 \times 10^6$
Al	221·752	$23\cdot5 \times 10^{-6}$	0·0269	$4\cdot2 \times 10^{-3}$	916·296	$0\cdot06894 \times 10^6$
Be	221·752	$13\cdot0 \times 10^{-6}$	0·04–0·06	$6\cdot0 \times 10^{-3}$	2012·504	$0\cdot29647 \times 10^6$
Co	69·036	$12\cdot3 \times 10^{-6}$	0·0624	$6\cdot0 \times 10^{-3}$	435·136	$0\cdot20684 \times 10^6$
Cu	393·296	$16\cdot5 \times 10^{-6}$	0·01673	$4\cdot3 \times 10^{-3}$	384·928	$0\cdot11031 \times 10^6$
Mg	153·553	$27\cdot0 \times 10^{-6}$	0·0440	$4\cdot2 \times 10^{-3}$	1037·632	$0\cdot04481 \times 10^6$
Mn	—	$22\cdot0 \times 10^{-6}$	1·60(α)	—	489·528	$0\cdot15857 \times 10^6$
Mo	142·256	$5\cdot1 \times 10^{-6}$	0·0570	$4\cdot6 \times 10^{-3}$	259·408	$0\cdot29647 \times 10^6$
Nb	52·300	$7\cdot2 \times 10^{-6}$	0·169	$3\cdot95 \times 10^{-3}$	255·224	$0\cdot10342 \times 10^6$
Ni	92·048	$12\cdot8 \times 10^{-6}$	0·0684	$6\cdot8 \times 10^{-3}$	451·872	$0\cdot20684 \times 10^6$
Pb	34·309	$29\cdot0 \times 10^{-6}$	0·206	$3\cdot36 \times 10^{-3}$	129·704	$0\cdot01378 \times 10^6$
Pd	70·291	$11\cdot7 \times 10^{-6}$	0·108	$3\cdot8 \times 10^{-3}$	246·856	$0\cdot11721 \times 10^6$
Pt	69·036	$9\cdot0 \times 10^{-6}$	0·106	$3\cdot92 \times 10^{-3}$	133·888	$0\cdot15168 \times 10^6$
Sn (white)	62·760	$23\cdot5 \times 10^{-6}$	0·128	$4\cdot2 \times 10^{-3}$	225·936	$0\cdot04688 \times 10^6$
Ta	54·392	$6\cdot5 \times 10^{-6}$	0·145	$3\cdot8 \times 10^{-3}$	142·256	$0\cdot18615 \times 10^6$
Ti	17·029	$8\cdot4 \times 10^{-6}$	0·550	$3\cdot5 \times 10^{-3}$	527·184	$0\cdot11721 \times 10^6$
U	25·104–27·196	\dagger	0·29(α)	$3\cdot4 \times 10^{-3}$	117·152	$0\cdot18960 \times 10^6$
V	30·962	$8\cdot3 \times 10^{-6}$	0·195	$2\cdot8 \times 10^{-3}$	497·896	$0\cdot13789 \times 10^6$
W	166·105	$4\cdot6 \times 10^{-6}$	0·055	$4\cdot6 \times 10^{-3}$	138·072	$0\cdot35852 \times 10^6$
Zn	110·876	$31\cdot0 \times 10^{-6}$	0·059	$4\cdot2 \times 10^{-3}$	393·296	$0\cdot09652 \times 10^6$
Zr	16·736	$5\cdot9 \times 10^{-6}$	0·446	$4\cdot4 \times 10^{-3}$	288·696	$0\cdot09307 \times 10^6$
Al alloys	167·360(±)	$21\cdot6 \times 10^{-6}$	0·035(+)	—	962·320	$0\cdot06895 \times 10^6$
Brass (70/30)	125·520	$19\cdot6 \times 10^{-6}$	0·062	$1\cdot5 \times 10^{-3}$	380·744	$0\cdot11032 \times 10^6$
Bronze (95/5)	86·680	$18\cdot0 \times 10^{-6}$	0·096	$1\cdot9 \times 10^{-3}$	376·560	$0\cdot11032 \times 10^6$
Monel (70/30)	25·104	$14\cdot4 \times 10^{-6}$	0·482	$1\cdot1 \times 10^{-3}$	543·920	$0\cdot17926 \times 10^6$
Fe–18Cr–8Ni stainless steel	14·644	$9\cdot5 \times 10^{-6}$	0·70	—	502·08	$0\cdot19305 \times 10^6$

*To convert into $\mu\Omega\text{cm}$ multiply by 100.†To convert into kN cm^{-2} multiply by 10^{-1} .‡ α -uranium 23×10^{-6} parallel to α -axis; $-3\cdot5 \times 10^{-6}$ parallel to b -axis; 17×10^{-6} parallel to c -axis. β -uranium 46×10^{-6} parallel to c -axis; 23×10^{-3} perpendicular to c -axis.

Table 21.3 Values of important constants in SI units

Quantity	Symbol	SI value
Molar gas constant	R	$8.314\ 3\ \text{J mol}^{-1}\ \text{K}^{-1}$
Boltzmann constant	k	$1.380\ 54 \times 10^{-23}\ \text{J K}^{-1}$
Avogadro's constant	N_A	$6.022\ 52 \times 10^{23}\ \text{mol}^{-1}$
Planck constant	h	$6.625\ 6 \times 10^{-34}\ \text{J s}$
Faraday constant	$F = N_A e$	$9.648\ 70 \times 10^4\ \text{C mol}^{-1}$
Mass of hydrogen atom	m_H	$1.673\ 43 \times 10^{-27}\ \text{kg}$
Proton mass	m_p	$1.672\ 52 \times 10^{-27}\ \text{kg}$
Neutron mass	m_n	$1.674\ 82 \times 10^{-27}\ \text{kg}$
Electron mass	m_e	$9.109\ 1 \times 10^{-31}\ \text{kg}$
	m_p/m_e	1.83610×10^3
Charge of positron	e	$1.602\ 10 \times 10^{-19}\ \text{C}$
Electron volt	1 eV	$1.602\ 10 \times 10^{-19}\ \text{J}$
Charge to mass ratio	e/m	$1.758\ 796 \times 10^{11}\ \text{C kg}^{-1}$
Molar volume of ideal gas at s.t.p. (101 325 Nm^{-2} and 273.15 K)	V_m	$2.241\ 36 \times 10^{-2}\ \text{m}^3\ \text{mol}^{-1}$
Speed of light	c	$2.997\ 925 \times 10^8\ \text{ms}^{-1}$
1st radiation constant	$c_1 = 2\pi hc^2$	$3.741\ 5 \times 10^{-16}\ \text{Wm}^2$
2nd radiation constant	$c_2 = hc/k$	$1.438\ 79 \times 10^{-2}\ \text{mK}$
Wien's radiation law $T_{\text{max}} = c_2/4.95511423$		$2.897\ 8 \times 10^{-3}\ \text{mK}$
Stefan-Boltzmann constant	σ	$5.669\ 7 \times 10^{-8}\ \text{Wm}^{-2}\ \text{K}^{-4}$
Standard gravity acceleration	g	$9.806\ 65\ \text{ms}^{-2}$
Absolute temperature of ice point	(0°C)	273.16 K
$RT_{298.16} \ln x$		$5709.4 \log x\ \text{J mol}^{-1}$
$(RT_{298.16}/F) \ln x$		$0.059\ 173 \log x\ \text{V}$

Data selected from 'Changing to the Metric System', *Metals and Materials*, Inst. of Metallurgists, 370, Dec. (1968).Table 21.4 Values of $(RT/F) \log x$ at various temperatures

$(RT/F) \ln x = \frac{8.3143\ T \times 2.3026}{96487} \log x$	
T (°C)	$(RT/F) \log x$ (V)
0	0.054 199
10	0.056 183
20	0.058 167
25	0.059 159
30	0.060 151
40	0.062 135
50	0.064 120
60	0.066 104
70	0.068 088
80	0.070 072
90	0.072 056
100	0.074 040

Table 21.5 Standard chemical potentials*

Notes. In the case of a single oxide (or hydroxide) existing in different allotropic states, indicated by the letters *a*, *b*, *c*, *d*, etc. the oxides are arranged in descending order of stability, i.e. in ascending order of standard chemical potentials (expressed for an identical chemical formula).

With reference to the degree of precision which can be attached to the numerical values given in this table, it may be taken that for each of these values all figures but the last are reasonably exact, while the concluding figure must always be treated with reserve.

Element	Symbol, denomination, crystal structure	μ° (kJ)	Element	Symbol, denomination, crystal structure	μ° (kJ)
Actinium	Ac	0	Antimony	Sb trig.	0
	Ac ³⁺	-753.12		Sb ₂ O ₃	
Aluminium	Al	0		senarmontite	
	Al ₂ O ₃ ·3H ₂ O			cub. <i>a</i>	-623.42
	hydrargillite <i>a</i>	-2320.45		Sb ₂ O ₃	
	Al ₂ O ₃ ·3H ₂ O			valentinite,	
	bayerite <i>b</i>	-2311.53		orthorhomb. <i>b</i>	-615.05
	Al ₂ O ₃ ·H ₂ O			Sb ₂ O ₄	
	bohmite <i>c</i>	-1820.04		orthorhomb.	-694.13
	Al ₂ O ₃			Sb ₂ O ₅	
	corundum α <i>d</i>	-1576.41		cub.	-838.89
	Al(OH) ₃			SbCl ₃	-324.76
	amorph. <i>e</i>	-1137.63		Sb ₂ S ₃	
	AlCl ₃	-636.80		amorph.	-133.89
	Al ₂ S ₃	-492.46		SbO ⁺	-175.73
	Al ₂ (SO ₄) ₃	-3091.93		HSbO ₂	-407.94
	AlN	-209.62		SbO ₂ ⁻	-345.18
	Al ₄ C ₃	-121.34		or Sb(OH) ₄ ⁻	-819.56
	Al ₂ SiO ₅			SbO ₂ ⁺	-274.05
	sillimanite	-2573.16		SbO ₃ ⁻	-514.34
	Al ₂ SiO ₅			or Sb(OH) ₆ ⁻	-1225.91
	andalusite	-2543.04		SbS ₂ ⁻	-54.39
	Al ₂ SiO ₅			SbH ₃	
	distheme (kyanite)	-2539.69		stibine	147.70
	Al ³⁺	-481.16		SbCl ₃	-302.50
	AlO ₂ ⁻	-839.77	Arsenic	As	
	or H ₂ AlO ₃ ⁻	-1076.96		trig.	0
Americium	Am	0		As ₂ O ₃	
	Am(OH) ₃			cub.	-576.05
	<i>a</i>	-1255.20		As ₂ O ₅	
	Am ₂ O ₃			amorph.	-772.37
	<i>b</i>	-1681.97		As ₂ S ₂	-134.52
	Am(OH) ₄			As ₂ S ₃	-135.81
	<i>a</i>	-1451.85		AsO ⁺	-163.59
	AmO ₂			HAsO ₂	-402.71
	cub. <i>b</i>	-966.50		or H ₃ AsO ₃	-639.90
	AmO ₂ OH			AsO ₂	-350.20
	or $\frac{1}{2}$ Am ₂ O ₅ ·H ₂ O	-1066.90		or H ₂ AsO ₃ ⁻	-587.39
	AmO ₃ (OH) ₂	-1117.90		HAsO ₃	-531.83
	or AmO ₃ ·H ₂ O	-1117.96		or H ₃ AsO ₄	-769.02
	Am ²⁺ (?)	-584.70		AsO ₃ ⁻	-511.33
	Am ³⁺	-671.53		or H ₂ AsO ₄ ⁻	-748.52
	Am ⁴⁺	-461.08		HAsO ₄ ²⁻	-707.10
	AmO ₂ ⁺	-813.79		AsO ₄ ³⁻	-635.97
	AmO ₂ ²⁺	-655.63		AsH ₃	175.73

*Data after M. Pourbaix, *Enthalpies Libres de Formations Standards*, à 25°C, Cebecor Rapport Technique, No. 87 (1960).
Abbreviations: aq., aqueous; cub., f.c.c.; cub.b., CaF₂ cubic type; cub.c., b.c.c.; g., gaseous; hex., hexahedral; liq., liquid; orthorh., orthorhombic; monoc., monoclinic; trig., trigonal; tetr., tetragonal.

Table 21.5 (continued)

Element	Symbol, denomination, crystal structure	μ° (kJ)	Element	Symbol, denomination, crystal structure	μ° (kJ)
Barium	BaH ₂ orthorh.	-132.21	Boron	B ₁₀ H ₁₄	271.96
	Ba			B	0
	Ba			B ₂ O ₃	
	cub.	0		<i>a</i>	-1198.42
	Ba(OH) ₂ ·8H ₂ O			B ₂ O ₃	
	monocl. <i>a</i>	-2789.89		vitreous <i>b</i>	-1187.80
	BaO			HBO ₂	-713.37
	cub. <i>b</i>	-528.44		or H ₃ BO ₃	-963.11
	BaO ₂ ·H ₂ O			H ₃ BO ₃ ⁻	-962.99
	tetr. <i>a</i>	-815.88		H ₂ BO ₃ ⁻	-910.44
	BaO ₂			HBO ₃ ²⁻	-838.01
	<i>b</i>	-568.19		BO ₃ ³⁻	-759.31
	BaF ₂	-1140.14		BO ₂ ⁻	-709.61
	BaCl ₂	-810.86		H ₂ B ₄ O ₇	-2651.48
	BaSO ₄	-1353.11		HB ₂ O ₇ ⁻	-2628.68
	Ba(NO ₃) ₂	-794.96		B ₄ O ₇ ²⁻	-2577.34
	Ba ₃ (PO ₄) ₂	-3951.37		B ₂ H ₆	82.76
Berkelium	BaCO ₃	-1138.88		B ₅ H ₉	168.40
	Ba(CN) ₂	-195.39		B ₁₀ H ₁₄	-297.06
Beryllium	Ba ²⁺	-560.66		BH	471.12
				BO	-81.67
Beryllium	Bk	0	Bromine	Br ₂ (liq.)	0
	Be			Br ⁻	-102.82
	hex.	0		Br ₂ ⁻	-105.73
	BeO·Be(OH) ₂			Br ₃ ⁻	-101.84
	'precipitated' <i>a</i>	-1414.15		Br ₃ (aq.)	4.09
	Be(OH) ₂			HBrO	-83.26
	'β', orthorh. <i>b</i>	-820.90		BrO ⁻	-33.47
	BeO			HBrO ₃	5.65
	hex.	-581.58		BrO ₃ ⁻	9.62
	Be(OH) ₂			HBr	-53.22
	'α' <i>d</i>	-817.97		Br ₂ (g.)	3.14
	BeCl ₂	-467.77	Cadmium	Cd	
	BeSO ₄	-1088.68		cadmium α, hex.	0
	Be ²⁺	-356.48		Cd	
	Be ₂ O ₃ ²⁺	-912.11		cadmium β	0.59
	Be ₂ O ₃ ⁻	-1246.83		Cd(OH) ₂	
	BeO ₂ ²⁻	-649.78		'inactive' trig. α	-473.34
	BeH ₂	298.32		Cd(OH) ₂	
Bismuth	Bi			'active' <i>b</i>	-470.03
	hex.	0		CdO	
	BiO	-182.00		cub. <i>c</i>	-225.06
	Bi ₂ O ₃			CdCl ₂	-342.59
	monocl. tetr.	-496.64		CdBr ₂	-293.47
	Bi(OH) ₃			CdS	-140.58
	amorph. β	-573.21		CdSO ₄	-820.02
	Bi ₄ O ₇	-973.83		CdCO ₃	-670.28
	Bi ₂ O ₄	-456.06		Cd(CN) ₂	207.94
	Bi ₂ O ₃	-383.11		Cd ²⁺	-77.74
	Bi ³⁺	62.05		HCdO ₂ ⁻	-361.92
	BiOH ²⁺	-163.72		CdCl ⁺	-216.73
	BiO ⁺	-144.52		CdCl ₂ (aq.)	-352.71
	BiH ₃			Cd(NH ₃) ₄ ²⁺	-224.81
	bismuthine	231.54		Cd(CN) ₄ ²⁻	464.42
				CdH	233.17

Table 21.5 (continued)

Element	Symbol, denomination, crystal structure	μ° (kJ)	Element	Symbol, denomination, crystal structure	μ° (kJ)
Calcium	CaH ₂ orthorh.	-149.79	Cerium	HCN	120.08
	Ca	0		CS ₂	65.06
	Ca(OH) ₂ rhomb. <i>a</i>	-896.76		CNCl	137.65
	CaO	-604.17		CCl ₄	-64.22
	CaO ₂	-598.31		COCl ₂	-210.50
	CaF ₂	-1161.90		Ce	0
	CaCl ₂	-750.19		Ce(OH) ₃	-1303.86
	CaBr ₂	-656.05		CeO ₂	-916.30
	CaI ₂	-529.69		cub.	-718.60
	CaS	-477.39		Ce ³⁺	-790.36
Californium	CaCO ₃ calcite rhomb.	-1128.76	Caesium	Ce(OH) ³⁺	-788.73
	CaCO ₃ aragonite, orthorh.	-1127.71		CeO ²⁺	-1025.92
	CaC ₂ O ₄ ·H ₂ O precipitated	-1508.75		or Ce(OH) ₂ ²⁺	-1025.92
	CaSO ₄ anhydrite	-1320.30		CsH	-30.54
	CaSO ₄ soluble α	-1311.77		cub.	0
	CaSO ₄ soluble β	-1307.33		Cs	-355.22
	Ca ²⁺	-553.04		cub. <i>c</i>	0
	Cf	0		CsOH	-274.47
Carbon	C	0		<i>a</i>	-327.19
	graphite, hex.	0		Cs ₂ O	-360.24
	diamond, cub.	2.87		trig. <i>b</i>	-387.02
	HCN	121.34		Cs ₂ O ₂	-282.04
	CS ₂	63.60	Chlorine	Cl ₂ (g.)	0
	CCl ₄	-68.74		HCl	-131.17
	CH ₃ OH	-174.47		Cl ⁻	-131.17
	HCHO	-129.70		Cl ₂ (aq.)	6.90
	HCO ₂ H	-356.06		HClO	-79.96
	HCO ₂ ⁻	-334.72		ClO ⁻	-37.24
	H ₂ C ₂ O ₄	-697.89		HClO ₂	0.29
	HC ₂ O ₄ ⁻	-690.86		ClO ₂ ⁻	11.46
	C ₂ O ₄ ²⁻	-666.93		HClO ₃	-2.59
	H ₂ CO ₃	-623.42		ClO ₃ ⁻	-2.59
Carbon	HCO ₃ ⁻	-587.06		HClO ₄	-10.33
	CO ₃ ²⁻	-528.10		ClO ₄ ⁻	-10.33
	HCN	112.13	Chromium	HCl	-95.27
	CN ⁻	165.69		Cl	105.40
	HCNO	-120.92		Cl ₂ O	93.72
	CNO ⁻	-98.74		ClO ₂	123.43
	CH ₄	-50.79		Cr	0
	CO	-137.27		Cr(OH) ₂	-587.85
	CO ₂	-394.38		Cr(OH) ₃	-900.82
	C ₂ N ₂	296.27		<i>a</i>	-1046.84
				Cr ₂ O ₃	-859.81
				<i>b</i>	-1014.12
				Cr(OH) ₃ · <i>n</i> H ₂ O	-502.08
				<i>c</i>	
				Cr(OH) ₄	
				CrO ₃	

Table 21.5 (continued)

<i>Element</i>	<i>Symbol, denomination, crystal structure</i>	μ° (kJ)	<i>Element</i>	<i>Symbol, denomination, crystal structure</i>	μ° (kJ)
	CrCl ₃	-493.71		Dy(OH) ₃	-1277.79
	Cr ²⁺	-176.15		DyCl ₃	-920.06
	Cr ³⁺	-215.48		DyI ₃	-599.15
	CrOH ²⁺	-430.95		Dy ³⁺	-681.16
	Cr(OH) ₂ ⁺	-632.66	Erbium	Er	
	CrO ₂ ⁻	-535.93		hex.	0
	CrO ₃ ²⁻	-603.42		Er(OH) ₃	
	H ₂ CrO ₄	-777.89		cub.	-1266.92
	HCrO ₄ ⁻	-773.62		ErCl ₃	-895.38
	CrO ₄ ²⁻	-736.80		ErI ₃	-580.74
	Cr ₂ O ₇ ²⁻	-1319.63		Er ³⁺	-664.67
Cobalt	Co		Europium	Eu	0
	hex.	0		Eu(OH) ₃	-1291.18
	Co(OH) ₂			Eu ²⁺	-655.21
	trig. <i>a</i>	-456.06		Eu ³⁺	-696.64
	CoO		Fluorine	F ₂	0
	cub. <i>b</i>	-205.02		HF(aq.)	-294.60
	Co ₃ O ₄			HF ₂ ⁻	-574.88
	cub.	-702.22		F ⁻	-276.48
	Co(OH) ₃	-596.64		HF(g.)	-270.70
	CoO ₂	-216.90		F	117.95
	CoCl ₂	-274.05		F ₂ O	40.58
	CoS		Gadolinium	Gd	
	α precipitated	-82.84		hex.	0
	CoSO ₄	-753.54		Gd(OH) ₃	-1288.67
	Co(NO ₃) ₂	-230.54		Gd ³⁺	-693.71
	CoCO ₃	-650.90		Gd(g)	322.17
Copper	Co ²⁺	-53.56	Gallium	Ga	
	HCoO ₂ ⁻	-347.15		tern.	0
	Co ³⁺	120.92		Ga ₂ O	-314.64
	Cu	0		Ga ₂ O ₃	
	Cu ₂ O			anh. monocl. or	
	cuprite, cub.	-146.36		orthorh. <i>a</i>	-992.44
	CuO			Ga(OH) ₃	
	mon. or cub. α	-127.19		or $\frac{1}{2}$ Ga ₂ O ₃ · 3H ₂ O	
	Cu(OH) ₂			hydroxide <i>b</i>	-832.62
	<i>b</i>	-356.90		Ga ²⁺	-87.86
	CuCl	-117.99		Ga ³⁺	-153.13
	Cu ₂ S	-86.19		GaOH ²⁺	-375.72
	Cu ₂ SO ₄	-652.70		GaO ⁺	-357.31
	CuCl ₂	-175.73		or Ga(OH) ₂ ⁺	-594.50
	CuS	-48.95		GaO ₂ ⁻	-507.52
	CuSO ₄	-661.91		or H ₂ GaO ₃ ⁻	-744.75
	CuCO ₃	-517.98		HGaO ₃ ²⁻	-686.18
	Cu ⁺	50.21		GaO ₃ ³⁻	-619.23
	Cu ²⁺	64.98	Germanium	Ge	0
	HCuO ₂ ⁻	-256.98		GeO hydr.	
	CuO ₂ ⁻	-182.00		<i>a</i>	-292.46
	CuCl ₂ ⁻	-242.25		GeO hydr.	
	CuH(?)	267.78		<i>b</i>	-262.34
Curium	Cm	0			
Dysprosium	Dy				
	hex.	0			

Table 21.5 (continued)

<i>Element</i>	<i>Symbol, denomination, crystal structure</i>	μ° (kJ)	<i>Element</i>	<i>Symbol, denomination, crystal structure</i>	μ° (kJ)
Germanium (continued)	GeO ₂		Iodine	In ²⁺	-51.88
	quad. <i>a</i>	-569.44		In ³⁺	-99.16
	GeO ₂			InOH ²⁺	-314.22
	'precipitated'			InO ₂ ⁻	-435.14
	hex. <i>b</i>	-552.29		InH	-188.28
	GeCl ₄	-497.90		I ₂	
	Ge ²⁺	0		orthorh.	0
	HGeO ₂ ⁻	-385.35		ICl	-13.56
	H ₂ GeO ₃	-781.57		ICl ₃	-22.59
	HGeO ₃ ⁻	-733.04		I ⁻	-51.67
Gold	GeO ₃ ²⁻	-660.65		I ₃ ⁻	-51.51
	GeH ₄	334.72		I ₅ ⁻	-28.87
	Au			I ₂ in solution	16.43
	cub.	0		I ⁺	130.92
	Au ₂ O ₃			or H ₂ IO ⁺	-106.27
	<i>a</i>	163.18		HIO	-98.32
	Au(OH) ₃			IO ⁻	-35.56
	<i>b</i>	289.95		HIO ₃	-139.49
	AuO ₂	200.83		IO ₃ ⁻	-134.93
	Au ⁺	163.18		HIO ₄	-62.84
	Au ³⁺	433.46		or H ₅ IO ₆	-537.23
	H ₇ AuO ₃	-258.57		IO ₄ ⁻	-53.14
	H ₂ AuO ₃ ⁻	-191.63		H ₄ IO ₆ ⁻	-518.31
	HAuO ₄ ²⁻	-115.48		HIO ₄ ²⁻	-243.13
	AuO ₃ ⁻	-24.27		or H ₃ IO ₆ ²⁻	-480.32
Hafnium	Hf			IO ₃ ¹⁻	-180.37
	Hex.	0		or H ₂ IO ₆ ¹⁻	-417.56
	HfO(OH) ₂			ICl	-16.74
	or HfO ₂ ·H ₂ O	-1361.89		HI	1.30
	HfO ₂			I ₂	19.37
	monocl. tetr.	-1055.20	Iridium	Ir	
	Hf ⁴⁺	-656.05		cub. f.c.	0
Holmium	HfO ²⁺	-902.49		Ir ₂ O ₃ ·xH ₂ O	
	Ho			hydr. sesquiox.	
	Hex.	0		μ° Ir ₂ O ₃	-175.73
	Ho(OH) ₃			Ir(OH) ₄	-591.53
	or $\frac{1}{2}$ Ho ₂ O ₃ ·3H ₂ O	-1272.35	Iron	Ir ³⁺	334.72
Hydrogen	Ho ³⁺	-671.11		IrO ₄ ²⁻	-196.65
	H ₂ (g.)	0		Fe	0
	H ₂ O	-237.19		Fe(OH) ₂	
	H ⁻	217.15		<i>a</i>	-483.54
	H ₂ (aq.)	17.70		FeO	
	H ⁺	0		wüstite <i>b</i>	-244.35
	OH ⁻	-157.30		Fe ₃ O ₄	
Indium	H ₁	203.24		magnetite, cub.	-1014.20
	In			Fe ₂ O ₃	
	tetr. f.c.	0		haematite, trig.	
	In ₂ O ₃			or cub. <i>a</i>	-740.99
	<i>a</i>	-821.74		Fe(OH) ₃	
	In(OH) ₃			<i>b</i>	-694.54
	<i>b</i>	-761.49		FeCl ₂	-302.08
	In ⁺	-13.39		FeS	-97.57
				FeSO ₄	-829.69

Table 21.5 (continued)

<i>Element</i>	<i>Symbol, denomination, crystal structure</i>	μ° (kJ)	<i>Element</i>	<i>Symbol, denomination, crystal structure</i>	μ° (kJ)
	FePO ₄	-1138.05		LiNO ₃	-389.53
	FeCO ₃	-673.88		Li ₂ CO ₃	-1132.44
	FeCl ₃	-336.39		Li ⁺	-293.80
	Fe ₂ S ₃	-246.86		LiOH	-451.12
	FeS ₂	-166.69		LiCl	-424.97
	Fe ²⁺	-84.94		Li ₂ SO ₄ (aq.)	-1329.59
	FeO ₂ H ⁻	-379.18		LiNO ₃ (aq.)	-404.30
	Fe ³⁺	-10.59		Li ₂ CO ₃ (aq.)	-1115.71
	FeOH ²⁺	-233.93		LiH	105.44
	Fe(OH) ₂ ⁺	-444.34	Lutetium	Lu	
	FeO ₂ ²⁻ (?)	-467.29		hex.	0
	FeCl ²⁺	-150.21		Lu(OH) ₃	-1259.38
Lanthanum	La	0		Lu ³⁺	-652.70
	La(OH) ₃ amorph. <i>a</i>	-1310.43	Magnesium	Mg	
	La ₂ O ₃ trig. <i>b</i>	-1786.15		hex.	0
	La ³⁺	-730.11		Mg(OH) ₂ trig. <i>a</i>	-833.75
Lead	Pb			MgO <i>b</i>	-569.57
	cub	0		MgO finely divided <i>c</i>	-566.14
	PbO tetr. <i>a</i>	-189.33		MgCl ₂	-592.33
	PbO orthorh. <i>b</i>	-188.49		MgOHCl	-732.20
	Pb(OH) ₂ <i>c</i>	-420.91		MgBr ₂	-499.15
	Pb ₃ O ₄	-617.56		MgS	-349.78
	Pb ₂ O ₃	-411.78		MgSO ₄	-1173.61
	PbO ₂	-218.99		Mg(NO ₃) ₂	-588.40
	PbCl ₂	-313.97		Mg ₃ (PO ₄) ₂	-3782.34
	PbBr ₂	-260.41		MgCO ₃	-1029.26
	PbI ₂	-173.76		MgNH ₄ PO ₄	-1631.76
	PbS	-92.68		Mg ²⁺	-456.01
	PbSO ₄	-811.24	Manganese	MgH	142.26
	Pb(NO ₃) ₂	-252.30		Mn	
	PbCO ₃	-626.34		α cub.	0
	PbCrO ₄	-851.86		Mn	
	Pb ²⁺	-24.31		γ tetr. f.c.	1.38
	HPbO ₂ ⁻	-338.90		Mn(OH) ₂ <i>a</i>	-614.63
	Pb ⁴⁺	302.50		MnO <i>b</i>	-363.17
	PbO ₂ ²⁻	-277.57		Mn ₂ O ₄ tetr.	-1280.30
	PbO ₄ ⁴⁻	-282.09		Mn ₂ O ₃ cub. <i>a</i>	-888.26
	PbH ₂	290.79		Mn(OH) ₃ monocl. <i>b</i>	-757.30
Lithium	Li	0		MnO ₂ β , pyrolusite	-464.84
	LiH cub.	-69.96		MnCl ₂	-441.41
	LiOH tetr. <i>a</i>	-443.09		MnS	-208.78
	Li ₂ O cub. <i>b</i>	-560.24		MnS precipitated	-223.01
	Li ₂ O ₂	-564.84		MnSO ₄	-955.96
	LiCl	-383.67			
	Li ₂ SO ₄	-1324.65			

Table 21.5 (continued)

<i>Element</i>	<i>Symbol, denomination, crystal structure</i>	μ° (kJ)	<i>Element</i>	<i>Symbol, denomination, crystal structure</i>	μ° (kJ)
Manganese (continued)	MnCO ₃	-817.55	Neptunium	Np	0
	Mn ²⁺	-227.61		orthorh.	
	HMnO ₂ ⁻	-505.85		Np(OH) ₃	-1248.92
	Mn ³⁺	-82.01		NpO ₂	
	MnO ₄ ²⁻	-503.75		cub. fc. <i>a</i>	-979.06
Mercury	MnO ₄ ⁻	-449.36		Np(OH) ₄	
	HgO			<i>b</i>	-1450.17
	red, orthorh. <i>a</i>	-58.53		Np ₂ O ₃	
	HgO			<i>a</i>	-2008.32
	yellow, orthorh. <i>b</i>	-58.40		NpO ₂ ·OH	
	Hg ₂ Cl ₂	-210.54		amorph. or	
	Hg ₂ Br ₂	-178.72		crystalline <i>b</i>	-1095.37
	Hg ₂ I ₂	-111.29		NpO ₂ (OH) ₂	-1206.25
	Hg ₂ S	-6.69		Np ³⁺	-537.23
	Hg ₂ SO ₄	-623.92		Np ⁴⁺	-522.58
	Hg ₂ CO ₃	-442.672		NpO ₂ ⁺	-924.66
	HgCl ₂	-185.77		NpO ₂ ²⁺	-813.79
	HgBr ₂	-147.36	Nickel	Ni	0
	HgI ₂			Ni(OH) ₂	
	<i>a</i>	-100.71		trig. <i>a</i>	-453.13
	HgI ₂			NiO	
	<i>b</i>	-96.65		cub. <i>b</i>	-214.64
	HgS			Ni ₃ O ₄ ·2H ₂ O	-1186.29
	cinnabar <i>a</i>	-48.83		Ni(OH) ₃	
	HgS			<i>a</i>	-541.83
	<i>b</i>	-46.23		Ni ₂ O ₃ ·H ₂ O	
	HgSO ₄	-589.94		<i>b</i>	-706.93
	Hg	0		NiO ₂ ·2H ₂ O	-689.52
	Hg ₂ ²⁺	152.09		NiS α	
	Hg ₂ ²⁺	164.77		<i>a</i>	-114.22
	Hg(OH) ₂	-274.89		NiS γ	
	HHgO ₂ ⁻	-190.04		<i>b</i>	-74.06
Molybdenum	HgH	220.08		NiSO ₄	-773.62
	Hg	31.76		Ni ²⁺	-47.49
	HgCl	58.58		HNiO ₂ ⁻	-349.22
	Mo		Niobium	Nb	
	cub. <i>c</i>	0		cub.	0
	MoO ₂			NbO	-378.65
	tetr.	-502.08		NbO ₂	-736.38
	H ₂ MoO ₄			Nb ₂ O ₃	-1766.49
	or MoO ₃ ·H ₂ O		Nitrogen	N ₂ O ₅	
	hex. <i>a</i>	-1186.96		hex.	133.89
	MoO ₃			HNO ₃ (liq.)	-79.91
	orthorh. <i>b</i>	-677.60		NH ₄ ⁺	-79.50
Neodymium	Mo ³⁺	-57.74		NH ₄ OH	-263.80
	HMoO ₄ ⁻	-893.70		N ₂ H ₄ H ₂ ⁺	94.14
	MoO ₄ ²⁻	-859.48		N ₂ H ₄	127.86
	Nd	0		NH ₂ OH ₂ ⁺	-56.65
	Nd(OH)			NH ₂ OH	-23.43
	<i>a</i>	-1294.11		HN ₃ (aq.)	298.32
	Nd ₂ O ₃			N ₃ ⁻	325.10
	tetr. or cub. <i>b</i>	-1759.79		N ₂ (aq.)	12.53
	Nd ³⁺	-703.75		H ₂ N ₂ O ₂	35.98

Table 21.5 (continued)

Element	Symbol, denomination, crystal structure	μ° (kJ)	Element	Symbol, denomination, crystal structure	μ° (kJ)
Nitrogen	NH_4O_2^-	76.15	Phosphorus	P_4H_2	66.94
	$\text{N}_2\text{O}_2^{2-}$	138.91		P	
	HNO_2	-53.64		red, cub. <i>a</i>	-13.81
	NO_2	-34.52		P	
	$\text{HNO}_3(\text{aq.})$	-110.58		white, cub. <i>b</i>	0
	NO_2^-	-110.58		P_2H_4	37.66
	NH_3	-16.64		PCl_3	-287.02
	$\text{HN}_3(\text{g.})$	328.44		H_3PO_2	-523.42
	N	340.90		H_2PO_2^-	-512.12
	$\text{N}_2(\text{g.})$	0		H_3PO_3	-856.88
	N_2O	103.60		H_2PO_3^-	-846.63
	NO	86.69		HPO_3^{2-}	-811.70
	NO_2	51.94		$\text{H}_2\text{P}_2\text{O}_6$	-1640.13
	N_2O_4	98.29		$\text{H}_3\text{P}_2\text{O}_6^{2-}$	-1627.58
	NOCl	66.36		$\text{H}_2\text{P}_2\text{O}_6^-$	-1611.68
	NOBr	82.42		$\text{HP}_2\text{O}_6^{3-}$	-1570.26
Osmium	Os			P_2O_5^+	-1513.35
	hex.	0		HPO_3	-902.91
	$\text{Os}(\text{OH})_4$	-683.58		H_2PO_4^-	-1147.25
	OsO_4			H_2PO_4^-	-1135.12
	monocl. <i>a</i>	-295.81		HPO_4^{2-}	-1094.12
	OsO_4			PO_4^{3-}	-1025.50
	<i>b</i>	-294.97		PH_3	18.24
	OsO_4^{2-}	-373.42		P_2	102.93
	H_2OsO_2	-529.86		P_4	24.35
	HOsO_5^-	-472.79		PCl_3	-286.27
	OsO_5^{3-}	-390.16		PCl_5	-324.55
	OsO_4	-294.09	Platinum	Pt	0
Oxygen	$\text{H}_2\text{O}(\text{liq.})$	-237.19		$\text{Pt}(\text{OH})_2$	-285.35
	$\text{H}_2\text{O}_2(\text{liq.})$	-113.97		PtO_2 hydrated	
	OH^-	-157.30		$\mu^\circ\text{PtO}_2$	-83.68
	$\text{H}_2\text{O}_2(\text{aq.})$	-131.67		PtO_3 hydrated	
	$\text{OH}(\text{aq.})$	35.69		$\mu^\circ\text{PtO}_3$	-66.94
	HO_2^-	-65.31		Pt^{2+}	229.28
	$\text{HO}_2(\text{aq.})$	12.55	Plutonium	Pu	0
	O_2^-	54.39		$\text{Pu}(\text{OH})_3$	-1172.36
	$\text{O}_2(\text{aq.})$	16.53		PuO_2	-979.06
	$\text{H}_2\text{O}(\text{g.})$	-228.59		$\text{Pu}(\text{OH})_4$	-1422.56
	$\text{OH}(\text{g.})$	37.36		$\text{PuO}_2 \cdot \text{OH}$	
	$\text{O}_1(\text{g.})$	230.09		or $\frac{1}{2}\text{Pu}_2\text{O}_5 \cdot \text{H}_2\text{O}$	-1032.19
	$\text{O}_2(\text{g.})$	0		$\text{PuO}_2(\text{OH})_2$	-1166.92
	$\text{O}_3(\text{g.})$	163.43		or $\text{PuO}_3 \cdot \text{H}_2\text{O}$	
Palladium	Pd_2H	-4.59		Pu^{3+}	-587.85
	Pd			Pu^{4+}	-494.55
	cub. f.c.c	0		PuO_2^+	-857.30
	$\text{Pd}(\text{OH})_2$			PuO_2^{2+}	-767.76
	<i>a</i>	-301.25	Polonium	Po	0
	PdO			PoO_2	> -194.97
	tetr. <i>b</i>	-60.25		PoO_3	-138.07
	$\text{Pd}(\text{OH})_4$	-528.02		Po^{2+}	125.52
	PdO_3	100.83		PoO_3^{2-}	-422.58
	Pd^{2+}	190.37		PoH_2	192.46

Table 21.5 (continued)

<i>Element</i>	<i>Symbol, denomination, crystal structure</i>	μ° (kJ)	<i>Element</i>	<i>Symbol, denomination, crystal structure</i>	μ° (kJ)
Potassium	KH			Re^{3+}	86.84
	cub.	-37.24		ReO_4^{2-}	-631.62
	K			ReO_4^-	-699.15
	cub. <i>c</i>	0	Rhodium	Rh	0
	KOH			Rh_2O	-83.68
	orthorh. <i>a</i>	-374.47		RhO	-75.31
	K_2O			Rh_2O_3	
	cub. <i>b</i>	-193.30		trig.	-219.66
	K_2O_2	-418.82		RhO_2	-62.76
	K_2O_3	-418.40		Rh^+	-58.58
	K_2O_4			Rh^{2+}	117.15
	tetr.	-416.73		Rh^{3+}	230.12
	KF	-533.13		RhO_4^{2-}	-62.76
	KCl	-408.32	Rubidium	RbH	
	KClO_3	-289.91		cub.	-30.54
	KClO_2	-304.18		Rb	
	KBr	-379.20		cub. <i>c</i>	0
	KI	-322.29		RbOH	
	K_2S	-404.17		trig. <i>a</i>	-364.43
	K_2SO_4	-1316.37		Rb_2O	
	KNO_3	-393.13		cub. <i>b</i>	-290.79
	KCN	-83.68		Rb_2O_2	
	K^+	-282.25		cub.	-349.78
	KOH	-439.58		Rb_2O_3	-386.60
Praseo- dymium	Pr			Rb_2O_4	-395.81
	hex. or cub. <i>c</i>	0		Rb^+	-282.21
	$\text{Pr}(\text{OH})_3$	-1295.78		RbOH	-439.53
	Pr_2O_3		Ruthenium	Ru	0
	trig. or cub.	-1770.25		$\text{Ru}(\text{OH})_3$	-497.90
	PrO_2			$\text{Ru}(\text{OH})_4$	-644.67
	cub.	-920.48		RuO_4	-109.20
	Pr^{3+}	-712.54		$\text{Ru}^{2+?}$	87.86
	Pr^{4+}	-436.60		RuO_4^{2-}	-257.73
Promethium	Pm	0		RuO_4^-	-200.83
	$\text{Pm}(\text{OH})_3$	-1292.86		H_7RuO_5	-341.41
	Pm^{3+}	-701.24		HRuO_5	-277.40
Protactinium	Pa	0	Samarium	Sm	
	tetr.			trig. or hex.	0
	PaO_2^+	958.14		$\text{Sm}(\text{OH})_3$	-1291.60
Radium	Ra	0		Sm^{2+}	-602.24
	RaO	-491.62		Sm^{3+}	-698.73
	Ra^{2+}	-562.75	Scandium	Sc	
Rhenium	Re			hex.	0
	hex.	0		$\text{Sc}(\text{OH})_3$	
	Re_2O_3 (hydr.)			amorph. <i>a</i>	-1228.00
	Re_2O_3	-579.94		Sc_2O_3	
	ReO_2	-372.38		<i>b</i>	-1631.76
	ReO_3			Sc^{3+}	-601.24
	cub.	-532.62		ScOH^{2+}	-801.44
	Re_2O_7		Selenium	Se	
	monocl.	-1057.30		γ	0
	Re^-	38.49			

Table 21.5 (continued)

<i>Element</i>	<i>Symbol, denomination, crystal structure</i>	μ° (kJ)	<i>Element</i>	<i>Symbol, denomination, crystal structure</i>	μ° (kJ)
Silicon	SeO ₂	-173.64	Sodium	Ag ₂ CO ₃	-437.14
	H ₂ Se	76.99		Ag ₂ CrO ₄	-647.26
	HSe ⁻	98.32		AgCN	164.01
	Se ²⁻	178.24		AgCNS	97.49
	H ₂ SeO ₃	-425.93		Ag ⁺	77.11
	HSeO ₃	-411.29		AgO ⁻	-22.97
	SeO ₂ ²⁻	-373.76		Ag ²⁺	268.19
	H ₂ SeO ₄	-441.08		AgO ⁺	-225.52
	HSeO ₄ ⁻	-452.71		Ag(S ₂ O ₃) ₂ ³⁻	-1035.96
	SeO ₄ ²⁻	-441.08		Ag(SO ₃) ₂ ³⁻	-943.07
	H ₂ Se	71.13		Ag(NH ₃) ₂ ⁺	-17.41
	Se ₂	88.49		Ag(CN) ₂ ⁻	-301.46
	Si			NaH	
	cub.	0		cub.	-37.66
	SiO ₂			Na	
	quartz, hex. <i>a</i>	-805.00		cub. <i>c</i>	0
	SiO ₂			NaOH.H ₂ O	
	crystalite <i>b</i>			<i>a</i>	-623.42
	cub.	-803.75		NaOH	
	SiO ₂			cub. <i>b</i>	-376.98
	tridymite <i>c</i>			Na ₂ O	
	cub.	-802.91		cub. <i>c</i>	-376.56
	SiO ₂			Na ₂ O ₂	
	vitreous <i>d</i>	-798.73		quad.	-430.12
Silver	H ₂ SiO ₃	-1022.99		NaO ₂	-194.56
	amorph. <i>e</i>	-572.79		NaF	-540.99
	SiCl ₄	-572.79		NaCl	-384.03
	H ₂ SiO ₃	-1012.53		NaBr	-347.69
	HSiO ₃ ⁻	-955.46		NaI	-237.23
	SiO ₃ ²⁻	-887.01		Na ₂ S	-362.33
	SiF ₆ ²⁻	-2138.02		Na ₂ SO ₄	-1266.83
	SiH ₄	-39.33		NaNO ₃	-365.89
	SiO	-137.11		Na ⁺	-261.87
	SiF ₄	-1506.24		NaOH	-419.17
	SiCl ₂	-569.86	Strontium	SrH ₂	
				orthorh.	-138.49
				Sr	
				cub.	0
				Sr(OH) ₂	-869.44
				SrO	
				cub.	-559.82
				SrO ₂	-581.58
				SrCl ₂	-781.15
				SrSO ₄	-1334.28
				Sr ²⁺	-557.31
			Sulphur	S	
				orthorh.	0
				S	
				monocl.	0.10
				H ₂ S	-27.36
				HS ⁻	12.59
				S ₂ ²⁻	91.87
				S ₂ ³⁻	82.63

Table 21.5 (continued)

<i>Element</i>	<i>Symbol, denomination, crystal structure</i>	μ° (kJ)	<i>Element</i>	<i>Symbol, denomination, crystal structure</i>	μ° (kJ)
Sulphur (continued)	S_2^{2-}	75.18	Terbium	Te^{2-}	220.50
	S_4^{2-}	69.52		Te_2^{2-}	-162.13
	S_8^{2-}	65.64		Te^{4+}	219.16
	$H_2S_2O_3$	-543.50		$HTeO_2^+$	-261.54
	HS_2O_3	-541.83		$HTeO_3^-$	-436.56
	$S_2O_2^{2-}$	-532.20		TeO_3^{1-}	-392.42
	$S_3O_6^{2-}$	-956.04		H_2TeO_4	-550.86
	$S_4O_6^{2-}$	-1022.15		or H_6TeO_6	-1025.24
	$H_2S_2O_4$	-585.76		$HTeO_4^-$	-515.75
	$HS_2O_4^-$	-591.65		or $H_3TeO_6^-$	-990.14
	$S_2O_4^{2-}$	-577.394		TeO_4^{1-}	-456.42
	$S_3O_6^{2-}$	-958.14		or $H_4TeO_6^{2-}$	-930.81
	H_2SO_3	-538.44		H_2Te	138.49
	HSO_3^-	-527.18		Te	159.41
	SO_3^{2-}	-485.76		Rc_2	121.34
	$S_2O_2^{2-}$	-790.78		Tb	
	$S_2O_3^{2-}$	-966.50		hex.	0
	H_2SO_4	-741.99		$Tb(OH)_3$	
	HSO_4^-	-752.87		cub.	-1287.84
	SO_4^{2-}	-741.99		Tb^{3+}	-692.03
	$S_2O_8^{2-}$	-1096.21	Thallium	Tl	
	H_2S	-33.02		hex.	0
	SO	53.47		$TlOH$	
	SO_2	-300.37		<i>a</i>	-190.37
	SO_3	-370.37		Tl_2O	
	SF_6	-991.61		<i>b</i>	-138.49
Tantalum	Ta			$Tl(OH)_3$	
	cub. <i>c</i>	0		<i>a</i>	-514.63
	Ta_2O_5			Tl_2O_3	
Technetium	orthorh.	-1910.00		<i>b</i>	-263.59
	Tc			$TlCl$	-184.89
	hex.	0		$TlBr$	-166.10
	TcO_2	-369.41		TlI	-124.26
	TcO_3	-460.53		$TlHO_3$	-199.16
	$Tc_2O_7 \cdot H_2O$			Tl_2SO_4	-823.41
	or $2HTcO_4$			Tl^+	-32.45
	<i>a</i>	-1182.15		Tl^{3+}	209.20
	Tc_2O_7			TlH	179.91
	<i>b</i>	-931.11	Thorium	Th	
	Tc^{2+}	-77.19		cub.	0
	$HTcO_4$	-629.50		ThO_2	
	TcO_4^-	-630.17		cub. <i>a</i>	-1164.83
Tellurium	Te	0		$Th(OH)_4$	
	TeO_2			<i>b</i>	-1585.74
	tetr. <i>a</i>	-273.30	Thulium	Th^{4+}	-733.04
	H_2TeO_3			Tm	
	or $TeO_2 \cdot H_2O$			hex.	0
	<i>b</i>	-478.48		$Tm(OH)_3$	-1265.24
	H_6TeO_6			Tm^{3+}	-659.40
	or $TeO_3 \cdot 3H_2O$		Tin	Sn	
	cub. or monocl.	-1025.24		tetr.	0
	H_2Te	142.67		Sn	4.60
	HTe^-	157.74			

Table 21.5 (continued)

Element	Symbol, denomination, crystal structure	μ° (kJ)	Element	Symbol, denomination, crystal structure	μ° (kJ)
Tin	SnO		Vanadium	U ₃ O ₈	-3363.94
	<i>a</i>	-257.32		UO ₃ ·H ₂ O	-1435.11
	Sn(OH) ₂			UO ₃ ·2H ₂ O	-1668.75
	<i>b</i>	-492.04		UO ₃	-1142.23
	SnO ₂			<i>c</i>	-520.49
	<i>a</i>	-515.47		U ³⁺	-579.07
	Sn(OH) ₄			U ⁴⁺	-809.60
	<i>b</i>	-951.86		UOH ³⁺	-994.12
	SnCl ₂	-302.08		UO ₂ ⁺	-989.10
	SnS	-82.42		V	0
	Sn(SO ₄) ₂	-1451.01		V ₂ O ₂	-790.78
	SnCl ₄	-474.05		V ₂ O ₃	-1133.86
	Sn ²⁺	-26.25		V ₂ O ₄	-1330.51
	SnOH ⁺	-253.55		V ₂ O ₅	-1439.30
	SnO ₂ H ⁻	-410.03		'evolved' <i>a</i>	-1431.08
	Sn ₃ O ₃ ²⁻	-590.28		V ₂ O ₅	-226.77
	Sn ⁴⁺	2.72		V ²⁺	-251.37
	SnO ₃ ⁻	-574.97		V(OH) ²⁺	-471.91
	SnH ₄	414.22		VO ⁺	-451.83
Titanium	Ti		Ytterbium	VO ²⁺	-456.06
	hex.	0		HVO ₂ ⁺	-662.66
	TiO	-489.19		HV ₂ O ₅ ⁻	-1508.96
	Ti ₂ O ₃			VO ₂ ⁺	-596.43
	trig. <i>a</i>	-1018.01		H ₃ V ₂ O ₇ ⁻	-1886.64
	Ti(OH) ₃			H ₂ VO ₄ ⁻	-1040.87
	<i>b</i>	-1049.79		HVO ₄ ²⁻	-986.59
	Ti ₃ O ₅	-2314.25		VO ₄ ³⁻	-921.00
	TiO ₂			VO ₄ ⁻	-853.12
	<i>a</i>	-888.39	Yttrium	Yb	
	TiO ₂ ·H ₂ O			cub. <i>c</i>	0
	<i>b</i>	-1058.51		Yb(OH) ₃	
	Ti ²⁺	-314.22		cub.	-1262.31
Tungsten	Ti ³⁺	-349.78	Yttrium	Yb ²⁺	-539.74
	TiO ²⁺	-577.39		Yb ³⁺	-656.05
	HTiO ₃ ⁻	-955.88		Y	
	TiO ₂ ⁺	-467.23		hex.	0
	W		Yttrium	Y(OH) ₃	
	cub. <i>c</i> and cub.	0		<i>a</i>	-1284.91
	WO ₂			Y ₂ O ₃	
Uranium	tetr.	-520.49		cub. <i>b</i>	-1681.97
	W ₂ O ₅	-1284.07	Zinc	Y ³⁺	-686.59
	WO ₃			Zn	0
	monocl.	-763.45		Zn(OH) ₂	
	WO ₄ ²⁻	-920.48		orthorh. ϵ , <i>a</i>	-559.09
	U			ZnO	
	UH ₃	-127.19		'inactive'	
	U	0		orthorh. <i>b</i>	-321.65
	UO	-514.63			
	U(OH) ₃	-1101.23			
	UO ₂				
	<i>a</i>	-1031.77			
	U(OH) ₄				
	<i>b</i>	-1471.09			

Table 21.5 (continued)

Element	Symbol, denomination, crystal structure	μ° (kJ)	Element	Symbol, denomination, crystal structure	μ° (kJ)
Zinc (continued)	Zn(OH) ₂		Zirconium	Zn(OH) ⁺	-329.28
	γ , white c	-557.78		HZnO ₂ ⁻	-464.01
	Zn(OH) ₂			ZnO ₂ ²⁻	-389.24
	β , orthorh. d	-557.04		Zr	
	ZnO			cub.	0
	'active' e	-316.67		Zr(OH) ₄	
	Zn(OH) ₂			a	-1548.08
	α , f	-552.02		ZrO(OH) ₂	
	Zn(OH) ₂			or ZrO ₂ ·H ₂ O	
	amorph. g	-551.68		b	-1303.32
	ZnCl ₂	-369.26		ZrO ₂	
	ZnBr ₂	-310.21		zircon monocl. c	-1036.38
	ZnS			ZrCl ₄	-874.46
	sphalerite	-198.32		Zr ⁴⁺	-594.13
	ZnSO ₄	-871.57		ZrO ²⁺	-843.08
	ZnCO ₃	-731.36		HZrO ₃ ⁻	-1203.74
	Zn ²⁺	-147.21			

Table 21.6 Standard electrode potentials against the standard hydrogen electrode* for inorganic systems at 25°C†

A Aqueous Acid Solutions

Electrode reaction	E° (V)	Electrode reaction	E° (V)
$\frac{1}{2}\text{N}_2 + e^- \rightarrow \text{N}_3^-$	-3.09	$\text{Sc}^{3+} + 3e^- \rightarrow \text{Sc}$	-2.08
$\text{Li}^+ + e^- \rightarrow \text{Li}$	-3.045	$\text{Pu}^{3+} + 3e^- \rightarrow \text{Pu}$	-2.07
$\text{K}^+ + e^- \rightarrow \text{K}$	-2.925	$\text{AlF}_6^{3-} + 3e^- \rightarrow \text{Al} + 6\text{F}^-$	-2.07
$\text{Rb}^+ + e^- \rightarrow \text{Rb}$	-2.925	$\text{Th}^{4+} + 4e^- \rightarrow \text{Th}$	-1.90
$\text{As}^+ + e^- \rightarrow \text{As}$	-2.923	$\text{Np}^{3+} + 3e^- \rightarrow \text{Np}$	-1.86
$\text{Ra}^{2+} + 2e^- \rightarrow \text{Ra}$	-2.92	$\text{Be}^{2+} + 2e^- \rightarrow \text{Be}$	-1.85
$\text{Ba}^{2+} + 2e^- \rightarrow \text{Ba}$	-2.90	$\text{U}^{3+} + 3e^- \rightarrow \text{U}$	-1.80
$\text{Sr}^{2+} + 2e^- \rightarrow \text{Sr}$	-2.89	$\text{Hf}^{4+} + 4e^- \rightarrow \text{Hf}$	-1.70
$\text{Ca}^{2+} + 2e^- \rightarrow \text{Ca}$	-2.87	$\text{Al}^{3+} + 3e^- \rightarrow \text{Al}$	-1.66
$\text{Na}^+ + e^- \rightarrow \text{Na}$	-2.714	$\text{Ti}^{2+} + 2e^- \rightarrow \text{Ti}$	-1.63
$\text{La}^{3+} + 3e^- \rightarrow \text{La}$	-2.52	$\text{Zr}^{4+} + 4e^- \rightarrow \text{Zr}$	-1.53
$\text{Ce}^{3+} + 3e^- \rightarrow \text{Ce}$	-2.48	$\text{SiF}_6^{2-} + 4e^- \rightarrow \text{Si} + 6\text{F}^-$	-1.2
$\text{Nd}^{3+} + 3e^- \rightarrow \text{Nd}$	-2.44	$\text{TiF}_6^{2-} + 4e^- \rightarrow \text{Ti} + 6\text{F}^-$	-1.19
$\text{Sm}^{3+} + 3e^- \rightarrow \text{Sm}$	-2.41	$\text{Mn}^{2+} + 2e^- \rightarrow \text{Mn}$	-1.18
$\text{Gd}^{3+} + 3e^- \rightarrow \text{Gd}$	-2.40	$\text{V}^{2+} + 2e^- \rightarrow \text{V}$	(-1.18)
$\text{Mg}^{2+} + 2e^- \rightarrow \text{Mg}$	-2.37	$\text{Nb}^{3+} + 3e^- \rightarrow \text{Nb}$	(-1.1)
$\text{Y}^{3+} + 3e^- \rightarrow \text{Y}$	-2.37	$\text{TiO}^{2+} + 2\text{H}^+ + 4e^- \rightarrow \text{Ti} + \text{H}_2\text{O}$	-0.89
$\text{Am}^{3+} + 3e^- \rightarrow \text{Am}$	-2.32	$\text{H}_3\text{BO}_3 + 3\text{H}^+ + 3e^- \rightarrow \text{B} + 3\text{H}_2\text{O}$	-0.87
$\text{Lu}^{3+} + 3e^- \rightarrow \text{Lu}$	-2.25	$\text{SiO}_2 + 4\text{H}^+ + 4e^- \rightarrow \text{Si} + 2\text{H}_2\text{O}$	-0.86
$\frac{1}{2}\text{H}_2 + e^- \rightarrow \text{H}^-$	-2.25	$\text{Ta}_2\text{O}_5 + 10\text{H}^+ + 10e^- \rightarrow$	
$\text{H}^+ + e^- \rightarrow \text{H(g.)}$	-2.10	$2\text{Ta} + 5\text{H}_2\text{O}$	-0.81

*This table of standard electrode potentials (or redox potentials) includes equilibria of the type $\text{M}^{z+} + ze^- = \text{M}$, i.e. the c.m.f. series of metals. Brackets indicate that the value of E° is unreliable.

†Data after Parsons, *Handbook of Electrochemical Constants*, Butterworths, London (1959).

Table 21.6 (continued)

Electrode reaction	E° (V)	Electrode reaction	E° (V)
$\text{AgNO}_2 + e^- \rightarrow \text{Ag} + \text{NO}_2^-$	0.564	$\text{ICl}_2^- + e^- \rightarrow \frac{1}{2} \text{I}_2 + 2\text{Cl}^-$	1.06
$\text{MnO}_4^- + e^- \rightarrow \text{MnO}_4^{2-}$	0.564	$\text{Br}_2(l.) + 2e^- \rightarrow 2\text{Br}^-$	1.065
$\text{PtBr}_4^- + 2e^- \rightarrow \text{Pt} + 4\text{Br}^-$	0.58	$\text{N}_2\text{O}_4 + 2\text{H}^+ + 2e^- \rightarrow 2\text{HNO}_2$	1.07
$\text{Sb}_2\text{O}_3 + 6\text{H}^+ + 4e^- \rightarrow$		$\text{Cu}^{2+} + 2\text{CN}^- + e^- \rightarrow \text{Cu}(\text{CN})_2^-$	1.12
$2\text{SbO}^+ + 3\text{H}_2\text{O}$	0.581	$\text{PuO}_2^+ + 4\text{H}^+ + e^- \rightarrow \text{Pu}^{4+} + 2\text{H}_2\text{O}$	1.15
$\text{CH}_3\text{OH}(aq.) + 2\text{H}^+ + 2e^- \rightarrow$		$\text{SeO}_4^{2-} + 4\text{H}^+ + 2e^- \rightarrow$	
$\text{CH}_4 + \text{H}_2\text{O}$	0.586	$\text{H}_2\text{SeO}_3 + \text{H}_2\text{O}$	1.15
$\text{PdBr}_4^{2-} + 2e^- \rightarrow \text{Pd} + 4\text{Br}^-$	0.6	$\text{NpO}_2^+ + e^- \rightarrow \text{NpO}_2^+$	1.15
$\text{RuCl}_3^- + 3e^- \rightarrow \text{Ru} + 5\text{Cl}^-$	0.60	$\text{CCl}_4 + 4\text{H}^+ + 4e^- \rightarrow \text{C} + 4\text{Cl}^- + 4\text{H}^+$	1.18
$\text{UO}_2^{2+} + 4\text{H}^+ + 2e^- \rightarrow \text{U}^{4+} + 2\text{H}_2\text{O}$	0.62	$\text{ClO}_4^- + 2\text{H}^+ + 2e^- \rightarrow \text{ClO}_3^- + \text{H}_2\text{O}$	1.19
$\text{PdCl}_2^- + 2e^- \rightarrow \text{Pd} + 4\text{Cl}^-$	0.62	$\text{IO}_3^- + 6\text{H}^+ + 5e^- \rightarrow \frac{1}{2} \text{I}_2 + 3\text{H}_2\text{O}$	1.195
$\text{Cu}^{2+} + \text{Br}^- + e^- \rightarrow \text{CuBr}$	0.640	$\text{ClO}_3^- + 3\text{H}^+ + 2e^- \rightarrow \text{HClO}_2 + \text{H}_2\text{O}$	1.21
$\text{Ag}_2\text{C}_2\text{H}_3\text{O}_2 + e^- \rightarrow \text{Ag} + \text{C}_2\text{H}_3\text{O}_2^-$	0.643	$\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}$	1.229
$\text{Ag}_2\text{SO}_4 + 2e^- \rightarrow 2\text{Ag} + \text{SO}_4^{2-}$	0.653	$\text{S}_2\text{Cl}_2 + 2e^- \rightarrow 2\text{S} + 2\text{Cl}^-$	1.23
$\text{Au}(\text{CNS})_2^- + 3e^- \rightarrow \text{Au} + 4\text{CNS}^-$	0.66	$\text{MnO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$	1.23
$\text{PtCl}_6^{2-} + 2e^- \rightarrow \text{PtCl}_4^{2-} + 2\text{Cl}^-$	0.68	$\text{Tl}^{3+} + 2e^- \rightarrow \text{Tl}^+$	1.25
$\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O}_2$	0.682	$\text{AmO}_2^+ + 4\text{H}^+ + e^- \rightarrow \text{Am}^{4+} + 2\text{H}_2\text{O}$	1.26
$\text{HN}_3 + 11\text{H}^+ + 8e^- \rightarrow 3\text{NH}_4^+$	0.69	$\text{N}_2\text{H}_5^+ + 3\text{H}^+ + 2e^- \rightarrow 2\text{NH}_4^+$	1.275
$\text{Te} + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{Te}$	0.70	$\text{ClO}_2 + \text{H}^+ + e^- \rightarrow \text{HClO}_2$	1.275
$2\text{NO} + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{N}_2\text{O}_2$	0.71	$\text{PdCl}_6^{2-} + 2e^- \rightarrow \text{PdCl}_4^{2-} + 2\text{Cl}^-$	1.288
$\text{H}_2\text{O}_2 + \text{H}^+ + e^- \rightarrow \text{OH} + \text{H}_2\text{O}$	0.72	$2\text{HNO}_2 + 4\text{H}^+ + 4e^- \rightarrow \text{N}_2\text{O} + 3\text{H}_2\text{O}$	1.29
$\text{PtCl}_4^{2-} + 2e^- \rightarrow \text{Pt} + 4\text{Cl}^-$	0.73	$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^- \rightarrow$	
$\text{C}_2\text{H}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{C}_2\text{H}_4$	0.73	$2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	1.33
$\text{H}_2\text{SeO}_3 + 4\text{H}^+ + 4e^- \rightarrow \text{Se} + 3\text{H}_2\text{O}$	0.74	$\text{NH}_3\text{OH}^+ + 2\text{H}^+ + 2e^- \rightarrow$	
$\text{NpO}_2^+ + 4\text{H}^+ + e^- \rightarrow \text{Np}^{4+} + 2\text{H}_2\text{O}$	0.75	$\text{NH}_4^+ + \text{H}_2\text{O}$	1.35
$(\text{CNS})_2 + 2e^- \rightarrow 2\text{CNS}^-$	0.77	$\text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^-$	1.360
$\text{IrCl}_6^{3-} + 3e^- \rightarrow \text{Ir} + 6\text{Cl}^-$	0.77	$2\text{NH}_3\text{OH}^+ + \text{H}^+ + 2e^- \rightarrow$	
$\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$	0.771	$\text{N}_2\text{H}_5^+ + 2\text{H}_2\text{O}$	1.42
$\text{Hg}_2^{2+} + 2e^- \rightarrow 2\text{Hg}$	0.789	$\text{Au}(\text{OH})_3 + 3\text{H}^+ + 3e^- \rightarrow \text{Au} + 3\text{H}_2\text{O}$	1.45
$\text{Ag}^+ + e^- \rightarrow \text{Ag}$	0.799	$\text{HIO} + \text{H}^+ + e^- \rightarrow \frac{1}{2} \text{I}_2 + \text{H}_2\text{O}$	1.45
$2\text{NO}_3^- + 4\text{H}^+ + 2e^- \rightarrow \text{N}_2\text{O}_4 + 2\text{H}_2\text{O}$	0.80	$\text{PbO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{Pb}^{2+} + 2\text{H}_2\text{O}$	1.455
$\text{Rh}^{3+} + 3e^- \rightarrow \text{Rh}$	(0.8)	$\text{Au}^{3+} + 3e^- \rightarrow \text{Au}$	1.50
$\text{OsO}_4(\text{colourless}) + 8\text{H}^+ + 8e^- \rightarrow$		$\text{HO}_2 + \text{H}^+ + e^- \rightarrow \text{H}_2\text{O}_2$	1.5
$\text{Os} + 4\text{H}_2\text{O}$	0.85	$\text{Mn}^{3+} + e^- \rightarrow \text{Mn}^{2+}$	1.51
$2\text{HNO}_2 + 4\text{H}^+ + 4e^- \rightarrow$		$\text{MnO}_4^- + 8\text{H}^+ + 5e^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	1.51
$\text{H}_2\text{N}_2\text{O}_2 + 2\text{H}_2\text{O}$	0.86	$\text{BrO}_3^- + 6\text{H}^+ + 5e^- \rightarrow \frac{1}{2} \text{Br}_2 + 3\text{H}_2\text{O}$	1.52
$\text{Cu}^{2+} + \text{I}^- + e^- \rightarrow \text{CuI}$	0.86	$\text{HBrO} + \text{H}^+ + e^- \rightarrow \frac{1}{2} \text{Br}_2 + \text{H}_2\text{O}$	1.59
$\text{AuBr}_4^- + 3e^- \rightarrow \text{Au} + 4\text{Br}^-$	0.87	$\text{Bi}_2\text{O}_3 + 4\text{H}^+ + 2e^- \rightarrow 2\text{BiO}^+ + 2\text{H}_2\text{O}$	1.59
$2\text{Hg}_2^{2+} + 2e^- \rightarrow \text{Hg}_2^{2+}$	0.920	$\text{H}_2\text{IO}_6 + \text{H}^+ + 2e^- \rightarrow \text{IO}_3^- + 3\text{H}_2\text{O}$	1.6
$\text{NO}_3^- + 3\text{H}^+ + 2e^- \rightarrow \text{HNO}_2 + \text{H}_2\text{O}$	0.94	$\text{Bk}^{4+} + e^- \rightarrow \text{Bk}^{3+}$	1.6
$\text{PuO}_2^{2+} + e^- \rightarrow \text{PuO}_2^+$	0.93	$\text{Ce}^{4+} + e^- \rightarrow \text{Ce}^{3+}$	1.61
$\text{NO}_3^- + 4\text{H}^+ + 4e^- \rightarrow \text{NO} + 2\text{H}_2\text{O}$	0.96	$\text{HClO} + \text{H}^+ + e^- \rightarrow \frac{1}{2} \text{Cl}_2 + \text{H}_2\text{O}$	1.63
$\text{AuBr}_2^- + e^- \rightarrow \text{Au} + 2\text{Br}^-$	0.96	$\text{AmO}_2^+ + e^- \rightarrow \text{AmO}_2^+$	1.64
$\text{Pu}^{4+} + e^- \rightarrow \text{Pu}^{3+}$	0.97	$\text{HClO}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{HClO} + \text{H}_2\text{O}$	1.64
$\text{Pt}(\text{OH})_2 + 2\text{H}^+ + 2e^- \rightarrow \text{Pt} + 2\text{H}_2\text{O}$	0.98	$\text{NiO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{Ni}^{2+} + 2\text{H}_2\text{O}$	1.68
$\text{Pd}^{2+} + 2e^- \rightarrow \text{Pd}$	0.987	$\text{PbO}_2 + \text{SO}_4^{2-} + 4\text{H}^+ + 2e^- \rightarrow$	
$\text{IrBr}_6^{3-} + e^- \rightarrow \text{IrBr}_6^{4-}$	0.99	$\text{PbSO}_4 + 2\text{H}_2\text{O}$	1.685
$\text{HNO}_2 + \text{H}^+ + e^- \rightarrow \text{NO} + \text{H}_2\text{O}$	1.00	$\text{AmO}_2^+ + 4\text{H}^+ + 3e^- \rightarrow$	
$\text{AuCl}_4^- + 3e^- \rightarrow \text{Au} + 4\text{Cl}^-$	1.00	$\text{Am}^{3+} + 2\text{H}_2\text{O}$	1.69
$\text{V}(\text{OH})_4^+ + 2\text{H}^+ + e^- \rightarrow \text{VO}^{2+} + 3\text{H}_2\text{O}$	1.00	$\text{MnO}_4^- + 4\text{H}^+ + 3e^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$	1.695
$\text{IrCl}_6^{3-} + e^- \rightarrow \text{IrCl}_6^{4-}$	1.017	$\text{Au}^+ + e^- \rightarrow \text{Au}$	(1.7)
$\text{H}_6\text{TeO}_6 + 2\text{H}^+ + 2e^- \rightarrow$		$\text{AmO}_2^+ + 4\text{H}^+ + 2e^- \rightarrow \text{Am}^{3+} + 2\text{H}_2\text{O}$	1.725
$\text{TeO}_2 + 4\text{H}_2\text{O}$	1.02	$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow 2\text{H}_2\text{O}$	1.77
$\text{N}_2\text{O}_4 + 4\text{H}^+ + 4e^- \rightarrow \text{NO} + 2\text{H}_2\text{O}$	1.03	$\text{Co}^{3+} + e^- \rightarrow \text{Co}^{2+}$	1.82
$\text{PuO}_2^{2+} + 4\text{H}^+ + 2e^- \rightarrow \text{Pu}^{4+} + 2\text{H}_2\text{O}$	1.04	$\text{FeO}_4^{2-} + 8\text{H}^+ + 3e^- \rightarrow \text{Fe}^{3+} + 4\text{H}_2\text{O}$	1.9

Table 21.6 (continued)

Electrode reaction	E° (V)	Electrode reaction	E° (V)
$\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}$	-0.763	$\text{HCOOH(aq.)} + 2\text{H}^+ + 2e^- \rightarrow$	
$\text{TlI} + e^- \rightarrow \text{Tl} + \text{I}^-$	-0.753	$\text{HCHO(aq.)} + \text{H}_2\text{O}$	0.056
$\text{Cr}^{3+} + 3e^- \rightarrow \text{Cr}$	-0.74	$\text{P} + 3\text{H}^+ + 3e^- \rightarrow \text{PH}_3(\text{g.})$	0.06
$\text{Te} + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{Te}$	-0.72	$\text{AgBr} + e^- \rightarrow \text{Ag} + \text{Br}^-$	0.095
$\text{TlBr} + e^- \rightarrow \text{Tl} + \text{Br}^-$	-0.658	$\text{TiO}^{2+} + 2\text{H}^+ + e^- \rightarrow \text{Ti}^{3+} + \text{H}_2\text{O}$	0.1
$\text{Nb}_2\text{O}_5 + 10\text{H}^+ + 10e^- \rightarrow$		$\text{Si} + 4\text{H}^+ + 4e^- \rightarrow \text{SiH}_4$	0.102
$2\text{Nb} + 5\text{H}_2\text{O}$	-0.65	$\text{C} + 4\text{H}^+ + 4e^- \rightarrow \text{CH}_4$	0.13
$\text{U}^{4+} + e^- \rightarrow \text{U}^{3+}$	-0.61	$\text{CuCl} + e^- \rightarrow \text{Cu} + \text{Cl}^-$	0.137
$\text{As} + 3\text{H}^+ + 3e^- \rightarrow \text{AsH}_3$	-0.60	$\text{S} + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{S}$	0.141
$\text{TlCl} + e^- \rightarrow \text{Tl} + \text{Cl}^-$	-0.557	$\text{Np}^{4+} + e^- \rightarrow \text{Np}^{3+}$	0.147
$\text{Ga}^{3+} + 3e^- \rightarrow \text{Ga}$	-0.53	$\text{Sn}^{4+} + 2e^- \rightarrow \text{Sn}^{2+}$	0.15
$\text{Sb} + 3\text{H}^+ + 3e^- \rightarrow \text{SbH}_3(\text{g.})$	-0.51	$\text{Sb}_2\text{O}_3 + 6\text{H}^+ + 6e^- \rightarrow 2\text{Sb} + 3\text{H}_2\text{O}$	0.152
$\text{H}_3\text{PO}_2 + \text{H}^+ + e^- \rightarrow \text{P} + 2\text{H}_2\text{O}$	-0.51	$\text{Cu}^{2+} + e^- \rightarrow \text{Cu}^+$	0.153
$\text{H}_3\text{PO}_3 + 2\text{H}^+ + e^- \rightarrow$		$\text{BiOCl} + 2\text{H}^+ + 3e^- \rightarrow$	
$\text{H}_3\text{PO}_2 + \text{H}_2\text{O}$	-0.50	$\text{Bi} + \text{H}_2\text{O} + \text{Cl}^-$	0.16
$\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe}$	-0.440	$\text{SO}_4^{2-} + 4\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{SO}_3 + \text{H}_2\text{O}$	0.17
$\text{Eu}^{3+} + e^- \rightarrow \text{Eu}^{2+}$	-0.43	$\text{HCHO(aq.)} + 2\text{H}^+ + 2e^- \rightarrow$	
$\text{Cr}^{3+} + e^- \rightarrow \text{Cr}^{2+}$	-0.41	$\text{CH}_3\text{OH(aq.)}$	0.19
$\text{Cd}^{2+} + 2e^- \rightarrow \text{Cd}$	-0.403	$\text{HgBr}_2^{2-} + 2e^- \rightarrow \text{Hg} + 4\text{Br}^-$	0.21
$\text{Se} + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{Se}$	-0.40	$\text{AgCl} + e^- \rightarrow \text{Ag} + \text{Cl}^-$	0.222
$\text{Ti}^{3+} + e^- \rightarrow \text{Ti}^{2+}$	(-0.37)	$\text{HAsO}_2(\text{aq.}) + 3\text{H}^+ + 3e^- \rightarrow$	
$\text{PbI}_2 + 2e^- \rightarrow \text{Pb} + 2\text{I}^-$	-0.365	$\text{As} + 2\text{H}_2\text{O}$	0.247
$\text{PbSO}_4 + 2e^- \rightarrow \text{Pb} + \text{SO}_4^{2-}$	-0.356	$\text{ReO}_3 + 4\text{H}^+ + 4e^- \rightarrow \text{Re} + 2\text{H}_2\text{O}$	0.252
$\text{In}^{3+} + 3e^- \rightarrow \text{In}$	-0.342	$\text{BiO}^+ + 2\text{H}^+ + 3e^- \rightarrow \text{Bi} + \text{H}_2\text{O}$	0.32
$\text{Ti}^+ + e^- \rightarrow \text{Ti}$	-0.336	$\text{HCNO} + \text{H}^+ + e^- \rightarrow \frac{1}{2}\text{C}_2\text{N}_2 + \text{H}_2\text{O}$	0.33
$\text{PtS} + 2\text{H}^+ + 2e^- \rightarrow \text{Pt} + \text{H}_2\text{S}$	-0.30	$\text{UO}_2^{2+} + 4\text{H}^+ + 2e^- \rightarrow \text{U}^{4+} + 2\text{H}_2\text{O}$	0.334
$\text{PbBr}_2 + 2e^- \rightarrow \text{Pb} + 2\text{Br}^-$	-0.280	$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$	0.337
$\text{Co}^{2+} + 2e^- \rightarrow \text{Co}$	-0.277	$\text{AgIO}_3 + e^- \rightarrow \text{Ag} + \text{IO}_3^-$	0.35
$\text{H}_3\text{PO}_4 + 2\text{H}^+ + 2e^- \rightarrow$		$\text{Fe}(\text{CN})_6^{3-} + e^- \rightarrow \text{Fe}(\text{CN})_6^{4-}$	0.36
$\text{H}_3\text{PO}_3 + \text{H}_2\text{O}$	-0.276	$\text{VO}^{2+} + 2\text{H}^+ + e^- \rightarrow \text{V}^{3+} + \text{H}_2\text{O}$	0.361
$\text{PbCl}_2 + 2e^- \rightarrow \text{Pb} + 2\text{Cl}^-$	-0.268	$\text{ReO}_4^- + 8\text{H}^+ + 7e^- \rightarrow \text{Re} + 4\text{H}_2\text{O}$	0.363
$\text{V}^{3+} + e^- \rightarrow \text{V}^{2+}$	-0.255	$\frac{1}{2}\text{C}_2\text{N}_2 + \text{H}^+ + e^- \rightarrow \text{HCN(aq.)}$	0.37
$\text{V}(\text{OH})_4^+ + 4\text{H}^+ + 5e^- \rightarrow \text{V} + 4\text{H}_2\text{O}$	-0.253	$2\text{H}_2\text{SO}_3 + 2\text{H}^+ + 4e^- \rightarrow$	
$\text{SnF}_6^{2-} + 4e^- \rightarrow \text{Sn} + 6\text{F}^-$	-0.25	$\text{S}_2\text{O}_3^{2-} + 3\text{H}_2\text{O}$	0.40
$\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}$	-0.250	$\text{RhCl}_6^{3-} + 3e^- \rightarrow \text{Rh} + 6\text{Cl}^-$	0.44
$\text{N}_2 + 5\text{H}^+ + 4e^- \rightarrow \text{N}_2\text{H}_5^+$	-0.23	$\text{Ag}_2\text{CrO}_4 + 2e^- \rightarrow 2\text{Ag} + \text{CrO}_4^{2-}$	0.446
$2\text{SO}_4^{2-} + 4\text{H}^+ + 2e^- \rightarrow$		$\text{H}_2\text{SO}_3 + 4\text{H}^+ + 4e^- \rightarrow \text{S} + 3\text{H}_2\text{O}$	0.45
$\text{S}_2\text{O}_6^{2-} + 2\text{H}_2\text{O}$	-0.22	$\text{Sb}_2\text{O}_3 + 2\text{H}^+ + 2e^- \rightarrow \text{Sb}_2\text{O}_4 + \text{H}_2\text{O}$	0.48
$\text{Mo}^{3+} + 3e^- \rightarrow \text{Mo}$	(-0.2)	$\text{Ag}_2\text{MoO}_4 + 2e^- \rightarrow 2\text{Ag} + \text{MoO}_4^{2-}$	0.49
$\text{CO}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{HCOOH(aq.)}$	-0.196	$\text{H}_2\text{N}_2\text{O}_2 + 6\text{H}^+ + 4e^- \rightarrow 2\text{NH}_3\text{OH}^+$	0.496
$\text{CuI} + e^- \rightarrow \text{Cu} + \text{I}^-$	-0.185	$\text{ReO}_4^- + 4\text{H}^+ + 3e^- \rightarrow$	
$\text{AgI} + e^- \rightarrow \text{Ag} + \text{I}^-$	-0.151	$\text{ReO}_2 + 2\text{H}_2\text{O}$	0.51
$\text{Sn}^{2+} + 2e^- \rightarrow \text{Sn}$	-0.136	$4\text{H}_2\text{SO}_4 + 4\text{H}^+ + 6e^- \rightarrow$	
$\text{O}_2 + \text{H}^+ + e^- \rightarrow \text{HO}_2$	-0.13	$\text{S}_2\text{O}_6^{2-} + 6\text{H}_2\text{O}$	0.51
$\text{Pb}^{2+} + 2e^- \rightarrow \text{Pb}$	-0.126	$\text{C}_2\text{H}_4 + 2\text{H}^+ + 2e^- \rightarrow \text{C}_2\text{H}_6$	0.52
$\text{GeO}_2 + 4\text{H}^+ + 4e^- \rightarrow \text{Ge} + 2\text{H}_2\text{O}$	-0.15	$\text{Cu}^+ + e^- \rightarrow \text{Cu}$	0.521
$\text{WO}_3(\text{colourless}) + 6\text{H}^+ + 6e^- \rightarrow$		$\text{TeO}_2(\text{colourless}) + 4\text{H}^+ + 4e^- \rightarrow$	
$\text{W} + 3\text{H}_2\text{O}$	-0.09	$\text{Te} + 2\text{H}_2\text{O}$	0.529
$2\text{H}_2\text{SO}_3 + \text{H}^+ + 2e^- \rightarrow$		$\text{I}_2 + 2e^- \rightarrow 2\text{I}^-$	0.536
$\text{HS}_2\text{O}_4^- + 2\text{H}_2\text{O}$	-0.08	$\text{I}_3^- + 2e^- \rightarrow 3\text{I}^-$	0.536
$\text{HgI}_2^{2-} + 2e^- \rightarrow \text{Hg} + 4\text{I}^-$	-0.04	$\text{Cu}^{2+} + \text{Cl}^- + e^- \rightarrow \text{CuCl}$	0.538
$2\text{H}^+ + 2e^- \rightarrow \text{H}_2$	0.000	$\text{AgBrO}_3 + e^- \rightarrow \text{Ag} + \text{BrO}_3^-$	0.55
$\text{Ag}(\text{S}_2\text{O}_3)_2^{3-} + e^- \rightarrow \text{Ag} + 2\text{S}_2\text{O}_3^{2-}$	0.01	$\text{TeOOH}^+ + 3\text{H}^+ + 4e^- \rightarrow \text{Te} + 2\text{H}_2\text{O}$	0.559
$\text{CuBr} + e^- \rightarrow \text{Cu} + \text{Br}^-$	0.033	$\text{H}_3\text{AsO}_4 + 2\text{H}^+ + 2e^- \rightarrow$	
$\text{UO}_2^{2+} + e^- \rightarrow \text{UO}_2^+$	0.05	$\text{HAsO}_2 + 2\text{H}_2\text{O}$	0.559

Table 21.6 (continued)

Electrode reaction	E° (V)	Electrode reaction	E° (V)
$\text{HN}_3 + 3\text{H}^+ + 2\text{e}^- \rightarrow \text{NH}_4^+ + \text{N}_2$	1.96	$\text{O(g.)} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$	2.42
$\text{Ag}^{2+} + \text{e}^- \rightarrow \text{Ag}^+$	1.98	$\text{F}_2 + 2\text{e}^- \rightarrow 2\text{F}^-$	2.65
$\text{S}_2\text{O}_8^{2-} + 2\text{e}^- \rightarrow 2\text{SO}_4^{2-}$	2.01	$\text{OH} + \text{H}^+ + \text{e}^- \rightarrow \text{H}_2\text{O}$	2.8
$\text{O}_3 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{O}_2 + \text{H}_2\text{O}$	2.07	$\text{H}_2\text{N}_2\text{O}_3 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$	2.85
$\text{F}_2\text{O} + 2\text{H}^+ + 4\text{e}^- \rightarrow 2\text{F}^- + \text{H}_2\text{O}$	2.1	$\text{F}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{HF(aq.)}$	3.06
$\text{Am}^{4+} + \text{e}^- \rightarrow \text{Am}^{3+}$	2.18		

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$\text{Ca(OH)}_2 + 2\text{e}^- \rightarrow \text{Ca} + 2\text{OH}^-$	-3.03	$\text{Te} + 2\text{e}^- \rightarrow \text{Te}^{2-}$	-1.14
$\text{Sr(OH)}_2 + 8\text{H}_2\text{O} + 2\text{e}^- \rightarrow$		$\text{PO}_4^{3-} + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow$	
$\text{Sr} + 2\text{OH}^- + 8\text{H}_2\text{O}$	-2.99	$\text{HPO}_3^{2-} + 3\text{OH}^-$	-1.12
$\text{Ba(OH)}_2 + 8\text{H}_2\text{O} + 2\text{e}^- \rightarrow$		$2\text{SO}_3^{2-} + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow$	
$\text{Ba} + 2\text{OH}^- + 8\text{H}_2\text{O}$	-2.97	$\text{S}_2\text{O}_4^{2-} + 4\text{OH}^-$	-1.12
$\text{H}_2\text{O} + \text{e}^- \rightarrow \text{H(g.)} + \text{OH}^-$	-2.93	$\text{ZnCO}_3 + 2\text{e}^- \rightarrow \text{Zn} + \text{CO}_3^{2-}$	-1.06
$\text{La(OH)}_3 + 3\text{e}^- \rightarrow \text{La} + 3\text{OH}^-$	-2.90	$\text{WO}_3 + 4\text{H}_2\text{O} + 6\text{e}^- \rightarrow \text{W} + 8\text{OH}^-$	-1.05
$\text{Lu(OH)}_3 + 3\text{e}^- \rightarrow \text{Lu} + 3\text{OH}^-$	-2.72	$\text{MoO}_4^{2-} + 4\text{H}_2\text{O} + 6\text{e}^- \rightarrow$	
$\text{Mg(OH)}_2 + 2\text{e}^- \rightarrow \text{Mg} + 2\text{OH}^-$	-2.69	$\text{Mo} + 8\text{OH}^-$	-1.05
$\text{Be}_2\text{O}_3 + 3\text{H}_2\text{O} + 4\text{e}^- \rightarrow$		$\text{Cd(CN)}_4^{2-} + 2\text{e}^- \rightarrow \text{Cd} + 4\text{CN}^-$	-1.03
$2\text{Be} + 6\text{OH}^-$	-2.62	$\text{Zn(NH}_3)_4^{2+} + 2\text{e}^- \rightarrow \text{Zn} + 4\text{NH}_3$	-1.03
$\text{Se(OH)}_3 + 3\text{e}^- \rightarrow \text{Se} + 3\text{OH}^-$	(-2.6)	$\text{FeS(a)} + 2\text{e}^- \rightarrow \text{Fe} + \text{S}^{2-}$	-1.01
$\text{HfO(OH)}_2 + \text{H}_2\text{O} + 4\text{e}^- \rightarrow$		$\text{In(OH)}_3 + 3\text{e}^- \rightarrow \text{In} + 3\text{OH}^-$	-1.0
$\text{Hf} + 4\text{OH}^-$	-2.50	$\text{PbS} + 2\text{e}^- \rightarrow \text{Pb} + \text{S}^{2-}$	-0.98
$\text{Th(OH)}_4 + 4\text{e}^- \rightarrow \text{Th} + 4\text{OH}^-$	-2.48	$\text{CNO}^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{CN}^- + 2\text{OH}^-$	-0.97
$\text{Pu(OH)}_3 + 3\text{e}^- \rightarrow \text{Pu} + 3\text{OH}^-$	-2.42	$\text{Ti}_2\text{S} + 2\text{e}^- \rightarrow \text{Ti} + \text{S}^{2-}$	-0.96
$\text{UO}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow \text{U} + 4\text{OH}^-$	-2.39	$\text{Pu(OH)}_4 + \text{e}^- \rightarrow \text{Pu(OH)}_3 + \text{OH}^-$	-0.95
$\text{H}_2\text{AlO}_3 + \text{H}_2\text{O} + 3\text{e}^- \rightarrow \text{Al} + 4\text{OH}^-$	-2.35	$\text{SnS} + 2\text{e}^- \rightarrow \text{Sn} + \text{S}^{2-}$	-0.94
$\text{H}_2\text{ZrO}_3 + \text{H}_2\text{O} + 4\text{e}^- \rightarrow \text{Zr} + 4\text{OH}^-$	-2.36	$\text{SO}_4^{2-} + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{SO}_3^{2-} + 2\text{OH}^-$	-0.93
$\text{U(OH)}_4 + \text{e}^- \rightarrow \text{U(OH)}_3 + \text{OH}^-$	-2.2	$\text{Se} + 2\text{e}^- \rightarrow \text{Se}^{2-}$	-0.92
$\text{U(OH)}_3 + 3\text{e}^- \rightarrow \text{U} + 3\text{OH}^-$	-2.17	$\text{HSnO}_3 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Sn} + 3\text{OH}^-$	-0.91
$\text{H}_2\text{PO}_2^- + \text{e}^- \rightarrow \text{P} + 2\text{OH}^-$	-2.05	$\text{HGeO}_3 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow \text{Ge} + 5\text{OH}^-$	-0.9
$\text{H}_2\text{BO}_3 + \text{H}_2\text{O} + 3\text{e}^- \rightarrow \text{B} + 4\text{OH}^-$	-1.79	$\text{Sn(OH)}_6^{2-} + 2\text{e}^- \rightarrow$	
$\text{SiO}_3^{2-} + 3\text{H}_2\text{O} + 4\text{e}^- \rightarrow \text{Si} + 6\text{OH}^-$	-1.70	$\text{HSnO}_2 + \text{H}_2\text{O} + 3\text{OH}^-$	-0.90
$\text{Na}_2\text{UO}_4 + 4\text{H}_2\text{O} + 2\text{e}^- \rightarrow$		$\text{P} + 3\text{H}_2\text{O} + 3\text{e}^- \rightarrow \text{PH}_3 + 3\text{OH}^-$	-0.89
$\text{U(OH)}_4 + 2\text{Na}^+ + 4\text{OH}^-$	-1.61	$\text{Fe(OH)}_2 + 2\text{e}^- \rightarrow \text{Fe} + 2\text{OH}^-$	-0.877
$\text{HPO}_3^{2-} + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow$		$\text{NiS(a)} + 2\text{e}^- \rightarrow \text{Ni} + \text{S}^{2-}$	-0.83
$\text{H}_2\text{PO}_2^- + 3\text{OH}^-$	-1.57	$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$	-0.828
$\text{Mn(OH)}_2 + 2\text{e}^- \rightarrow \text{Mn} + 2\text{OH}^-$	-1.55	$\text{Cd(OH)}_2 + 2\text{e}^- \rightarrow \text{Cd} + 2\text{OH}^-$	-0.809
$\text{MnCO}_3 + 2\text{e}^- \rightarrow \text{Mn} + \text{CO}_3^{2-}$	-1.48	$\text{FeCO}_3 + 2\text{e}^- \rightarrow \text{Fe} + \text{CO}_3^{2-}$	-0.756
$\text{ZnS} + 2\text{e}^- \rightarrow \text{Zn} + \text{S}^{2-}$	-1.44	$\text{CdCO}_3 + 2\text{e}^- \rightarrow \text{Cd} + \text{CO}_3^{2-}$	-0.74
$\text{Cr(OH)}_3 + 3\text{e}^- \rightarrow \text{Cr} + 3\text{OH}^-$	-1.3	$\text{Co(OH)}_2 + 2\text{e}^- \rightarrow \text{Co} + 2\text{OH}^-$	-0.73
$\text{Zn(CN)}_4^{2-} + 2\text{e}^- \rightarrow \text{Zn} + 4\text{CN}^-$	-1.26	$\text{HgS} + 2\text{e}^- \rightarrow \text{Hg} + \text{S}^{2-}$	-0.72
$\text{Zn(OH)}_2 + 2\text{e}^- \rightarrow \text{Zn} + 2\text{OH}^-$	-1.245	$\text{Ni(OH)}_2 + 2\text{e}^- \rightarrow \text{Ni} + 2\text{OH}^-$	-0.72
$\text{H}_2\text{GaO}_3 + \text{H}_2\text{O} + 3\text{e}^- \rightarrow$		$\text{Ag}_2\text{S} + 2\text{e}^- \rightarrow 2\text{Ag} + \text{S}^{2-}$	-0.69
$\text{Ga} + 4\text{OH}^-$	-1.22	$\text{AsO}_3^{3-} + 2\text{H}_2\text{O} + 3\text{e}^- \rightarrow \text{As} + 4\text{OH}^-$	-0.68
$\text{ZnO}_2^{2-} + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Zn} + 4\text{OH}^-$	-1.216	$\text{AsO}_4^{3-} + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow$	
$\text{CrO}_2 + 2\text{H}_2\text{O} + 3\text{e}^- \rightarrow \text{Cr} + 4\text{OH}^-$	-1.2	$\text{AsO}_2^- + 4\text{OH}^-$	-0.67
$\text{CdS} + 2\text{e}^- \rightarrow \text{Cd} + \text{S}^{2-}$	-1.21	$\text{Fe}_2\text{S}_3 + 2\text{e}^- \rightarrow 2\text{FeS} + \text{S}^{2-}$	-0.67
$\text{HV}_6\text{O}_{17}^{3-} + 16\text{H}_2\text{O} + 30\text{e}^- \rightarrow$		$\text{SbO}_2 + 2\text{H}_2\text{O} + 3\text{e}^- \rightarrow \text{Sb} + 4\text{OH}^-$	-0.66
$6\text{V} + 33\text{OH}^-$	-1.15	$\text{CoCO}_3 + 2\text{e}^- \rightarrow \text{Co} + \text{CO}_3^{2-}$	-0.64

* E° for unit activity OH^- against the standard hydrogen electrode (unit activity H^+)

Table 21.6 (continued)

Electrode reaction	E° (V)	Electrode reaction	E° (V)
$\text{Cd}(\text{NH}_3)_2^{2+} + 2e^- \rightarrow \text{Cd} + 4\text{NH}_3$	-0.597	$\text{N}_2\text{H}_4 + 4\text{H}_2\text{O} + 2e^- \rightarrow 2\text{NH}_4\text{OH} + 2\text{OH}^-$	0.1
$\text{ReO}_4^- + 2\text{H}_2\text{O} + 3e^- \rightarrow \text{ReO}_2 + 4\text{OH}^-$	-0.594	$\text{Ir}_2\text{O}_3 + 3\text{H}_2\text{O} + 6e^- \rightarrow \text{Ir} + 6\text{OH}^-$	0.1
$\text{ReO}_4^- + 4\text{H}_2\text{O} + 7e^- \rightarrow \text{Re} + 8\text{OH}^-$	-0.584	$\text{Co}(\text{NH}_3)_6^{3+} + e^- \rightarrow \text{Co}(\text{NH}_3)_6^{2+}$	0.1
$2\text{SO}_3^{2-} + 3\text{H}_2\text{O} + 4e^- \rightarrow \text{S}_2\text{O}_3^{2-} + 6\text{OH}^-$	-0.58	$\text{Mn}(\text{OH})_3 + e^- \rightarrow \text{Mn}(\text{OH})_2$	0.1
$\text{ReO}_2 + \text{H}_2\text{O} + 4e^- \rightarrow \text{Re} + 4\text{OH}^-$	-0.576	$\text{Pt}(\text{OH})_2 + 2e^- \rightarrow \text{Pt} + 2\text{OH}^-$	0.15
$\text{TeO}_3^{2-} + 3\text{H}_2\text{O} + 4e^- \rightarrow \text{Te} + 6\text{OH}^-$	-0.57	$\text{Co}(\text{OH})_3 + e^- \rightarrow \text{Co}(\text{OH})_2 + \text{OH}^-$	0.17
$\text{Fe}(\text{OH})_3 + e^- \rightarrow \text{Fe}(\text{OH})_2 + \text{OH}^-$	-0.56	$\text{PbO}_2 + \text{H}_2\text{O} + 2e^- \rightarrow \text{PbO}(\text{red}) + 2\text{OH}^-$	0.248
$\text{O}_2 + e^- \rightarrow \text{O}_2^-$	-0.56	$\text{IO}_3^- + 3\text{H}_2\text{O} + 6e^- \rightarrow \text{I}^- + 6\text{OH}^-$	0.26
$\text{Cu}_2\text{S} + 2e^- \rightarrow 2\text{Cu} + \text{S}^{2-}$	-0.54	$\text{PuO}_2(\text{OH})_2 + e^- \rightarrow \text{PuO}_2\text{OH} + \text{OH}^-$	0.26
$\text{HPbO}_2^- + \text{H}_2\text{O} + 2e^- \rightarrow \text{Pb} + 3\text{OH}^-$	-0.54	$\text{Ag}(\text{SO}_3)_2^{2-} + e^- \rightarrow \text{Ag} + 2\text{SO}_3^{2-}$	0.30
$\text{PbCO}_3 + 2e^- \rightarrow \text{Pb} + \text{CO}_3^{2-}$	-0.506	$\text{ClO}_2^- + \text{H}_2\text{O} + 2e^- \rightarrow \text{ClO}_2 + 2\text{OH}^-$	0.33
$\text{S} + 2e^- \rightarrow \text{S}^{2-}$	-0.48	$\text{Ag}_2\text{O} + \text{H}_2\text{O} + 2e^- \rightarrow 2\text{Ag} + 2\text{OH}^-$	0.344
$\text{Ni}(\text{NH}_3)_6^{2+} + 2e^- \rightarrow \text{Ni} + 6\text{NH}_3(\text{aq.})$	-0.47	$\text{ClO}_2 + \text{H}_2\text{O} + 2e^- \rightarrow \text{ClO}_2^- + 2\text{OH}^-$	0.36
$\text{NiCO}_3 + 2e^- \rightarrow \text{Ni} + \text{CO}_3^{2-}$	-0.454	$\text{Ag}(\text{NH}_3)_2^+ + e^- \rightarrow \text{Ag} + 2\text{NH}_3$	0.373
$\text{Bi}_2\text{O}_3 + 3\text{H}_2\text{O} + 6e^- \rightarrow 2\text{Bi} + 6\text{OH}^-$	-0.44	$\text{TeO}_4^{2-} + \text{H}_2\text{O} + 2e^- \rightarrow \text{TeO}_3^{2-} + 2\text{OH}^-$	0.4
$\text{Cu}(\text{CN})_2 + e^- \rightarrow \text{Cu} + 2\text{CN}^-$	-0.43	$\text{O}_2 + \text{H}_2\text{O} + e^- \rightarrow \text{OH}^- + \text{HO}_2^-$	0.4
$\text{Hg}(\text{CN})_2 + 2e^- \rightarrow \text{Hg} + 4\text{CN}^-$	-0.37	$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^-$	0.401
$\text{SeO}_3^{2-} + 3\text{H}_2\text{O} + 4e^- \rightarrow \text{Se} + 6\text{OH}^-$	-0.366	$\text{Ag}_2\text{CO}_3 + 2e^- \rightarrow 2\text{Ag} + \text{CO}_3^{2-}$	0.47
$\text{Cu}_2\text{O} + \text{H}_2\text{O} + 2e^- \rightarrow 2\text{Cu} + 2\text{OH}^-$	-0.358	$\text{NiO}_2 + 2\text{H}_2\text{O} + 2e^- \rightarrow \text{Ni}(\text{OH})_2 + 2\text{OH}^-$	0.49
$\text{Ti}(\text{OH}) + e^- \rightarrow \text{Ti} + \text{OH}^-$	-0.345	$\text{IO}^- + \text{H}_2\text{O} + 2e^- \rightarrow \text{I}^- + 2\text{OH}^-$	0.49
$\text{Ag}(\text{CN})_2 + e^- \rightarrow \text{Ag} + 2\text{CN}^-$	-0.31	$2\text{AgO} + \text{H}_2\text{O} + 2e^- \rightarrow \text{Ag}_2\text{O} + 2\text{OH}^-$	0.57
$\text{CuNS} + e^- \rightarrow \text{Cu} + \text{NS}^-$	-0.27	$\text{MnO}_4^{2-} + 2\text{H}_2\text{O} + 2e^- \rightarrow \text{MnO}_2 + 4\text{OH}^-$	0.60
$\text{HO}_2^- + \text{H}_2\text{O} + e^- \rightarrow \text{OH} + 2\text{OH}^-$	-0.24	$\text{RuO}_4^- + e^- \rightarrow \text{RuO}_4^{2-}$	0.60
$\text{CrO}_4^{2-} + 4\text{H}_2\text{O} + 3e^- \rightarrow \text{Cr}(\text{OH})_3 + 5\text{OH}^-$	-0.13	$\text{BrO}_3^- + 3\text{H}_2\text{O} + 6e^- \rightarrow \text{Br}^- + 6\text{OH}^-$	0.61
$\text{Cu}(\text{NH}_3)_2^+ + e^- \rightarrow \text{Cu} + 2\text{NH}_3$	-0.12	$\text{ClO}_2^- + \text{H}_2\text{O} + 2e^- \rightarrow \text{ClO}_2 + 2\text{OH}^-$	0.66
$2\text{Cu}(\text{OH})_2 + 2e^- \rightarrow \text{Cu}_2\text{O} + 2\text{OH}^- + \text{H}_2\text{O}$	-0.080	$\text{H}_3\text{IO}_6^{2-} + 2e^- \rightarrow \text{IO}_3^- + 3\text{OH}^-$	0.7
$\text{O}_2 + \text{H}_2\text{O} + 2e^- \rightarrow \text{HO}_2^- + \text{OH}^-$	-0.076	$2\text{NH}_2\text{OH} + 2e^- \rightarrow \text{N}_2\text{H}_4 + 2\text{OH}^-$	0.73
$\text{Ti}(\text{OH})_3 + 2e^- \rightarrow \text{TiOH} + 2\text{OH}^-$	-0.05	$\text{Ag}_2\text{O}_3 + \text{H}_2\text{O} + 2e^- \rightarrow 2\text{AgO} + 2\text{OH}^-$	0.74
$\text{AgCN} + e^- \rightarrow \text{Ag} + \text{CN}^-$	-0.017	$\text{BrO}^- + \text{H}_2\text{O} + 2e^- \rightarrow \text{Br}^- + 2\text{OH}^-$	0.76
$\text{MnO}_2 + 2\text{H}_2\text{O} + 2e^- \rightarrow \text{Mn}(\text{OH})_2 + 2\text{OH}^-$	-0.05	$\text{HO}_2^- + \text{H}_2\text{O} + 2e^- \rightarrow 3\text{OH}^-$	0.88
$\text{NO}_3^- + \text{H}_2\text{O} + 2e^- \rightarrow \text{NO}_2^- + 2\text{OH}^-$	0.01	$\text{ClO}^- + \text{H}_2\text{O} + 2e^- \rightarrow \text{Cl}^- + 2\text{OH}^-$	0.89
$\text{HOSOs}^- + 4\text{H}_2\text{O} + 8e^- \rightarrow \text{Os} + 9\text{OH}^-$	0.02	$\text{FeO}_4^{2-} + 2\text{H}_2\text{O} + 3e^- \rightarrow \text{FeO}_2 + 4\text{OH}^-$	0.9
$\text{Rh}_2\text{O}_3 + 3\text{H}_2\text{O} + 6e^- \rightarrow 2\text{Rh} + 6\text{OH}^-$	0.04	$\text{ClO}_2 + e^- \rightarrow \text{ClO}_2^-$	1.16
$\text{SeO}_4^{2-} + \text{H}_2\text{O} + 2e^- \rightarrow \text{SeO}_3^{2-} + 2\text{OH}^-$	0.05	$\text{O}_3 + \text{H}_2\text{O} + 2e^- \rightarrow \text{O}_2 + 2\text{OH}^-$	1.24
$\text{Pd}(\text{OH})_2 + 2e^- \rightarrow \text{Pd} + 2\text{OH}^-$	0.07	$\text{OH} + e^- \rightarrow \text{OH}^-$	2.0
$\text{S}_2\text{O}_6^{2-} + 2e^- \rightarrow 2\text{S}_2\text{O}_3^{2-}$	0.08		
$\text{HgO}(\text{red}) + \text{H}_2\text{O} + 2e^- \rightarrow \text{Hg} + 2\text{OH}^-$	0.098		

Table 21.7 Reference electrodes

Electrode	Electrode equilibrium	Potential at 25°C (vs. S.H.E.; V)
Calomel (Hg/Hg ₂ Cl ₂ , Cl ⁻)	Hg ₂ Cl ₂ + 2e ⇌ 2Hg + 2Cl ⁻	$E = 0.2677 - 0.0591 \log a_{\text{Cl}^-}$ Solution E_{calomel} $E_{\text{calomel}} + \text{liquid junction}$ Temp. coeff. 0.1 mol dm ⁻³ KCl 0.3337 0.336 -0.06mV/°C 1.0 mol dm ⁻³ KCl 0.280 0.283 -0.24mV/°C Sat. KCl 0.241 0.244 -0.65mV/°C $E = 0.6151 - 0.0295 \log a_{\text{SO}_4^{2-}}$ $E = 0.2224 - 0.0591 \log a_{\text{Cl}^-}$ Average temp. coeff. ≈ -0.6mV/°C* 0.1 mol dm ⁻³ KCl, $E = 0.2881$ V 1.0 mol dm ⁻³ KCl, $E = 0.2224$ V Sea-water $E \approx 0.250$ V
Mercury/mercurous sulphate (Hg/HgSO ₄ , SO ₄ ²⁻)	HgSO ₄ + 2e ⇌ Hg + SO ₄ ²⁻	
Silver/silver chloride (Ag/AgCl, Cl ⁻)	AgCl + e ⇌ Ag + Cl ⁻	$E = 0.2224 - 0.0591 \log a_{\text{Cl}^-}$ Average temp. coeff. ≈ -0.6mV/°C* 0.1 mol dm ⁻³ KCl, $E = 0.2881$ V 1.0 mol dm ⁻³ KCl, $E = 0.2224$ V Sea-water $E \approx 0.250$ V
Copper/copper sulphate (Cu/CuSO ₄ , Cu ²⁺)	Cu ²⁺ + 2e ⇌ Cu	$E = 0.340 + 0.0295 \log a_{\text{Cu}^{2+}}$; for sat. CuSO ₄ , $E = 0.318$ V; for practical electrodes $E \approx 0.30$ V
Quinhydrone	Quinone + H ₂ ⇌ hydroquinone	$E = E_x^\circ - 0.0591 \text{ pH}$, and $E_x^\circ = 0.6990$ at 25°C E_x° contains a term due to diffusion potentials and is not a thermodynamic constant
Antimony/antimony oxide (Sb/Sb ₂ O ₃ , H ⁺)	Sb ₂ O ₃ + 6H ⁺ + 6e ⇌ 2Sb + 3H ₂ O	$E = 0.1445 - 0.0591 \text{ pH}$
Mercury/mercuric oxide (Hg/HgO, OH ⁻)	HgO + 2H ⁺ + 2e ⇌ Hg + H ₂ O	$E = 0.926 - 0.0591 \text{ pH}$ (for pH determinations in alkaline solution)
Lead dioxide/lead sulphate (Pb/PbO ₂ /PbSO ₄ , SO ₄ ²⁻)	PbO ₂ + 4H ⁺ + SO ₄ ²⁻ + 2e ⇌ PbSO ₄ + 2H ₂ O	$E = 1.685 + 0.0295 \log 4m^3\gamma_s/\alpha_s^2$, where γ_s and α_s are the stoichiometric mean activity coefficient of sulphuric acid and the activity of water, respec- tively, at molality m of H ₂ SO ₄
		Solution E 0.1 mol dm ⁻³ H ₂ SO ₄ +1.565 1.1 mol dm ⁻³ H ₂ SO ₄ +1.632 6.1 mol dm ⁻³ H ₂ SO ₄ +1.735
Zn/ZnSO ₄	Zn ²⁺ + 2e ⇌ Zn	$E = -0.763 + 0.0295 \log a_{\text{Zn}^{2+}}$
Zn/sea-water	Mixed potentials approximating to $E_{\text{M}^{2+}/\text{M}}^\circ$	$E \approx -0.80$ V
Zn/artificial sea-water	Mixed potentials approximating to $E_{\text{M}^{2+}/\text{M}}^\circ$	$E \approx -0.81$ V
Cd/sea-water	Mixed potentials approximating to $E_{\text{M}^{2+}/\text{M}}^\circ$	$E \approx -0.52$ V
Cd/artificial sea-water	Mixed potentials approximating to $E_{\text{M}^{2+}/\text{M}}^\circ$	$E \approx -0.54$ V

*Variation of $E_{\text{Ag}^\circ/\text{AgCl}^\circ}$ with temperature: Temp., °C

	35	45	55	70	95	125	150	200
E° , V	0.215 70	0.208 28	0.200 42	0.187 82	0.165 1	0.133 0	0.103 2	0.034 8

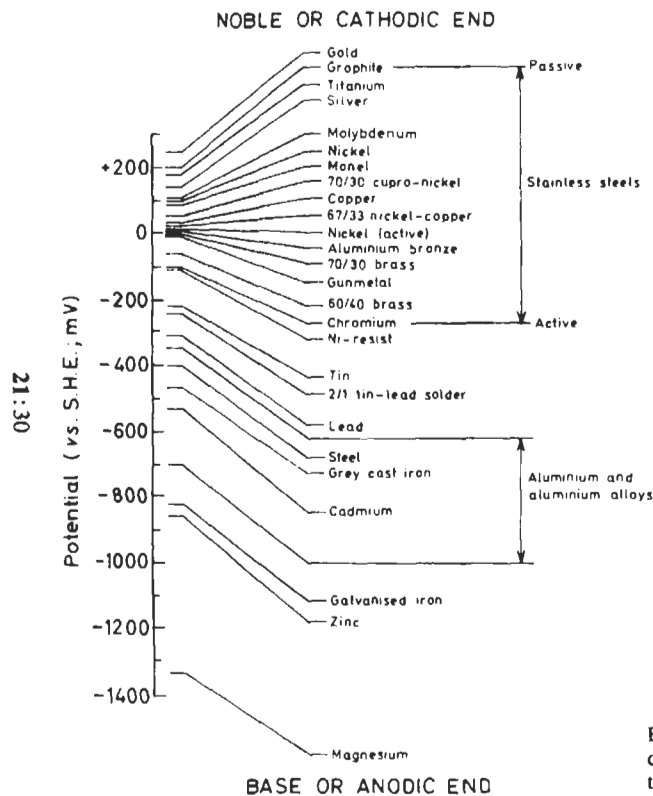


Fig. 21.1 Practical galvanic series of metals and alloys showing potentials on the hydrogen scale. (Note that the potentials shown are typical values that will vary according to the nature of the solution.) (after Butler, G. and Ison, H. C. K., *Corrosion and its Prevention in Water*, Leonard Hill, London (1966))

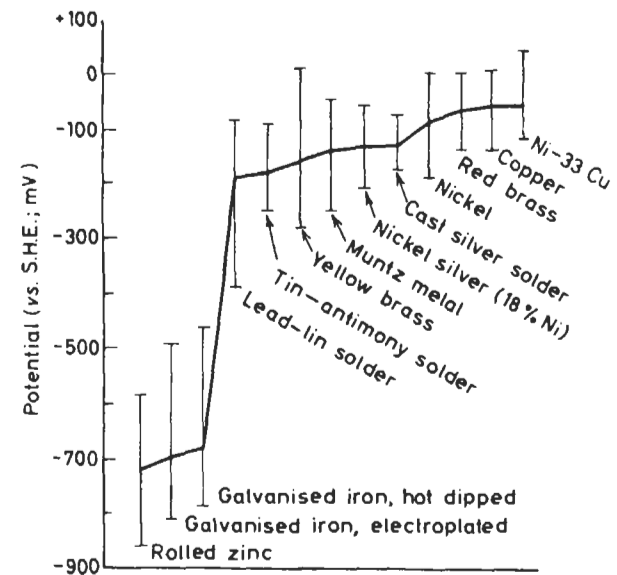


Fig. 21.2 Galvanic series showing ranges of potentials of metals and alloys in flowing hot domestic water at 71°C (Long Island, N.Y.). Potentials measured weekly for three months and then monthly for a period of ten months. (After Butler, G. and Ison, H. C. K., *Corrosion and its Prevention in Water*, Leonard Hill, London (1966))

Table 21.8 Galvanic series of some commercial metals and alloys in sea-water*

Noble or cathodic ↑	Platinum
	Gold
	Graphite
	Titanium
	Silver
	{Chlorimet 3 (62Ni-18Cr-18Mo)
	{Hastelloy C (62Ni-17Cr-15Mo)
	{18/8 Mo stainless steel (passive)
	{18/8 stainless steel (passive)
	{Chromium stainless steel 11-30% Cr (passive)
	{Inconel (passive) (Ni-13Cr-7Fe)
	{Nickel (passive)
	Silver solder
	{Monel (Ni-30Cu)
	{Cupro-nickels (Cu-10 to 40Ni)
	{Bronzes (Cu-Sn)
	{Copper
	{Brasses (Cu-Zn)
	{Chlorimet 2 (66Ni-32Mo-1Fe)
	{Hastelloy B (60Ni-30Mo-6Fe-1Mn)
	{Inconel (active)
	{Nickel (active)
Active or anodic ↓	Tin
	Lead
	Lead-tin solders
	{18/8 Mo stainless steel (active)
	{18/8 stainless steel (active)
	Ni-Resist (high nickel cast iron)
	Chromium stainless steel, 13% Cr (active)
	{Cast iron
	{Steel or iron
	2024 aluminium (Al-4.5Cu-1.5Mg-0.6Mn)
	Cadmium
	Commercially pure aluminium (1100)
	Zinc
	Magnesium and magnesium alloys

*Data after Fontana, M. G., and Greene, N. D., *Corrosion Engineering*, McGraw Hill (1967).**Table 21.9** Stoichiometric mean molal activity coefficients (γ_{\pm}) for aqueous inorganic electrolytes at 25°C*

Electrolyte	Molality									
	0.001	0.005	0.01	0.05	0.1	0.2	0.5	1.0	3	7
AgNO ₃		0.925	0.897	0.793	0.734	0.657	0.536	0.429	0.252	0.142
AlCl ₃				0.447	0.337	0.305	0.331	0.539		
Al(NO ₃) ₃					0.204	0.157		0.190	0.102	
Al ₂ (SO ₄) ₃					0.035	0.023	0.014	0.018		
Ba(OH) ₂		0.773	0.712	0.526	0.443	0.370				
CaCl ₂	0.889	0.789	0.731	0.583	0.518	0.472	0.448	0.500	1.483	18.28
Ca(NO ₃) ₂	0.88	0.77	0.71	0.545	0.485	0.426	0.363	0.336	0.380	0.690

*Data after Parsons, *Handbook of Electrochemical Constants*, Butterworths, London (1959).

Table 21.9 (continued)

Electrolyte	Molality									
	0.001	0.005	0.01	0.05	0.1	0.2	0.5	1.0	3	7
Cd(NO ₃) ₂					0.513	0.464	0.425	0.433		
CdCl ₂	0.819	0.623	0.524	0.304	0.228	0.164	0.101	0.0669	0.0352	
CdSO ₄	0.726	0.505	0.399	0.206	0.150	0.102	0.061	0.041	0.033	
CoCl ₂					0.522	0.479	0.462	0.531		
Co(NO ₃) ₂					0.518	0.471	0.445	0.490		
CrCl ₃					0.331	0.298	0.314	0.481		
Cr(NO ₃) ₃					0.319	0.285	0.291	0.401		
Cr ₂ (SO ₄) ₃					0.0458	0.0300	0.0190	0.0208		
CuCl ₂	0.888	0.783	0.723	0.577	0.508	0.455	0.411	0.417	0.520	
Cu(NO ₃) ₂					0.511	0.460	0.426	0.455	0.903	4.21
CuSO ₄	0.74	0.573	0.438	0.217	0.154	0.104	0.062	0.043		
FeCl ₂					0.518	0.473	0.450	0.506		
HCl	0.965	0.928	0.904	0.830	0.796	0.767	0.757	0.809	1.316	4.37
HNO ₃	0.965	0.927	0.902	0.823	0.791	0.754	0.720	0.724	0.909	
H ₂ SO ₄	0.830	0.639	0.544	0.340	0.265	0.209	0.156	0.132	0.142	0.317
HClO ₄					0.803	0.778	0.769	0.823	1.448	7.44
KCl	0.965	0.927	0.902	0.816	0.770	0.718	0.649	0.604	0.569	
KNO ₃	0.965	0.926	0.898	0.799	0.739	0.663	0.545	0.443	0.269	
K ₂ SO ₄	0.885	0.777	0.711	0.525	0.441	0.360	0.264			
KOH				0.824	0.798	0.760	0.732	0.756	1.081	2.88
MgCl ₂					0.529	0.489	0.481	0.570	2.32	
Mg(NO ₃) ₂	0.882	0.771	0.712	0.554	0.523	0.481	0.470	0.537	1.452	
MnCl ₂					0.516	0.469	0.440	0.479	0.934	2.25
MnSO ₄					0.150	0.106	0.064	0.044	0.038	
NH ₄ Cl		0.924	0.896	0.808	0.770	0.718	0.649	0.603	0.561	0.566
NH ₄ NO ₃		0.925	0.897	0.799	0.740	0.677	0.582	0.504	0.368	0.261
NaCl	0.965	0.928	0.903	0.822	0.778	0.735	0.681	0.657	0.714	
NaNO ₃	0.966	0.929	0.905	0.821	0.762	0.703	0.617	0.548	0.437	
Na ₂ SO ₄	0.877	0.778	0.714	0.536	0.445	0.365	0.266	0.201	0.137	
NaCNS					0.787	0.750	0.715	0.712	0.814	
NaH ₂ PO ₄					0.744	0.675	0.563	0.468	0.320	
NaOH			0.905	0.818	0.766	0.727	0.690	0.678	0.784	1.603
NiCl ₂					0.522	0.479	0.464	0.536	1.692	
NiSO ₄					0.150	0.105	0.063	0.042	0.035	
PbCl ₂	0.859	0.704	0.612							
UO ₂ Cl ₂					0.544	0.510	0.517	0.620	1.551	
UO ₂ (NO ₃) ₂					0.551	0.520	0.542	0.689	2.03	
UO ₂ SO ₄					0.150	0.102	0.0611	0.0439	0.0383	
ZnCl ₂	0.88	0.77	0.71	0.56	0.515	0.462	0.394	0.339	0.287	0.499
Zn(NO ₃) ₂					0.531	0.489	0.473	0.535	1.363	
ZnSO ₄	0.700	0.477	0.387	0.202	0.150	0.104	0.063	0.043	0.041	

Note. Where experimental data are unavailable, mean ionic activity coefficients (up to an ionic strength I of 0.1) in water at 25°C can be calculated from the formula

$$-\log \gamma_{\pm} = 0.509 z_+ z_- \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.020I \right)$$

where z_+ , z_- are valencies of the ions, and I (the ionic strength) = $\frac{1}{2} \sum m_i z_i^2$.

Table 21.10 Differential diffusion coefficients for dilute aqueous solutions at 25°C*

<i>Solution</i>	<i>Range of concentration (mol dm⁻³)</i>	<i>Range of $D \times 10^5$ (cm²s⁻¹)†</i>
AgNO ₃	0.628×10^{-3}	1.768–1.701
BaCl ₂	0.542×10^{-3}	1.387–1.261
CaCl ₂	0.501×10^{-3}	1.336–1.179
CaCl ₂	0–3.5	1.336–1.195
CsCl	0.1287×10^{-3}	2.406–1.946
Cs ₂ SO ₄	0.472×10^{-3}	1.569–1.424
HBr	0–1.0	3.403–3.869
HCl	0–4.0	3.339–5.17
KBr	0–4.0	2.018–2.434
KCl (4°C)	16.6558×10^{-3}	1.080–1.042
(20°C)	0.1121×10^{-3}	1.765–1.689
(25°C)	0.5276×10^{-3}	1.996–1.852
(30°C)	0.1236×10^{-3}	2.233–2.139
KCl	0–3.5	1.995–2.152
KI	0–3.5	2.001–2.533
KNO ₃	0.919×10^{-3}	1.931–1.855
K ₄ Fe(CN) ₆	0.556×10^{-3}	1.473–1.178
LaCl ₃	0.26×10^{-3}	1.294–1.021
LiBr	0–3.5	1.379–1.693
LiCl	0.1100×10^{-3}	1.368–1.313
LiCl	0–3.5	1.368–1.464
LiNO ₃	0–4.0	1.337–1.292
Li ₂ SO ₄	0.573×10^{-3}	1.041–0.946
MgCl ₂	0.400×10^{-3}	1.251–1.164
MgSO ₄	0.636×10^{-3}	0.849–0.702
NaBr	0–2.5	1.627–1.702
NaCl	0.1473×10^{-3}	1.612–1.542
NaCl	0–4.5	1.612–1.607
NaI	0–3.0	1.616–1.992
Na ₂ SO ₄	0.479×10^{-3}	1.230–1.124
NH ₄ Cl	0–4.5	1.996–2.257
RbCl	0.1110×10^{-3}	2.057–1.969
SrCl ₂	0.774×10^{-3}	1.336–1.208

*Data after Parsons, *Handbook of Electrochemical Constants*, Butterworths, London (1959).

† $D \times 10^5 \text{ m}^2 \text{ s}^{-1}$.

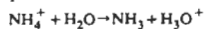
Table 21.11 Ionisation constants of water and weak electrolytes and variation with temperatureA. Ionisation constants of water ($pK_w = -\log K_w$)

Temperature (°C)	$-\log K_w$	Temperature (°C)	$-\log K_w$
0	14.9435	35	13.6801
5	14.7338	40	13.5348
10	14.5346	45	13.3960
15	14.3463	50	13.2617
20	14.1669	55	13.1369
25	13.9965	60	13.0171
30	13.8330		

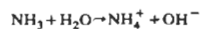
B. Ionisation constants of weak electrolytes and their temperature variation
 $pK_a = -\log K_a = A_1/T - A_2 + A_3T$

Aqueous solution	pK_a at 25°C	A_1	A_2	A_3
Acetic acid	4.756	1170.48	3.1649	0.013 399
Ammonium ion	9.245	2835.76	0.6322	0.001 225
Benzoic acid	4.201	1590.2	6.394	0.017 65
Boric acid	9.234	2237.94	3.305	0.016 883
n-Butyric acid	4.820	1033.39	2.6215	0.013 334
Carbonic acid K_1	6.352	3404.71	14.8435	0.032 786
Carbonic acid K_2	10.329	2902.39	6.4980	0.023 79
Chloroacetic acid	2.861	1049.05	5.0273	0.014 654
Citric acid K_1	3.128	1255.6	4.5635	0.011 673
Citric acid K_2	4.761	1585.2	5.4460	0.016 399
Citric acid K_3	6.396	1814.9	6.3664	0.022 389
Formic acid	3.752	1342.85	5.2743	0.015 168
Glycine K_1	2.350	1332.17	5.8870	0.012 643
Glycine K_2	9.780	2686.95	0.5103	0.004 286
Lactic acid	3.860	1286.49	4.8607	0.014 776
Malonic acid K_1	2.855	—	—	—
Malonic acid K_2	5.696	1703.31	6.5810	0.022 014
Oxalic acid K_1	1.271	—	—	—
Oxalic acid K_2	4.266	1423.8	6.5007	0.020 095
Phosphoric acid K_1	2.148	799.31	4.5535	0.013 486
Phosphoric acid K_2	7.198	1979.5	5.3541	0.019 840
o-Phthalic acid K_1	2.950	561.57	1.2843	0.007 883
o-Phthalic acid K_2	5.408	2175.83	9.5508	0.025 694
Succinic acid K_1	4.207	1206.25	3.3266	0.011 697
Succinic acid K_2	5.638	1679.13	5.7043	0.019 153
Sulphamic acid	0.988	3792.8	24.122	0.041 544
Sulphanilic acid	3.227	1143.71	1.2979	0.002 314
Tartaric acid K_1	3.033	1525.59	6.6558	0.015 336
Tartaric acid K_2	4.366	1765.35	7.3015	0.019 276
Trimethylammonium ion	9.800	541.4	-12.611	-0.015 525

Note. All values are with reference to the molarity scale. Data for bases are expressed as acidic ionisation constants, e.g. for ammonia we quote pK at $25^\circ = 9.245$ for the ammonium ion



The basic ionisation constant of the reaction



is obtained from the relation

$$pK_a(\text{acidic}) + pK_b(\text{basic}) = pK_w(\text{water})$$

$pK_w(\text{water})$ being 13.9965 at 25°C .

Table 21.12 Tafel constants for hydrogen evolution from aqueous solution*

The Tafel equation for a cathodic reaction is $\eta_c = a - b \log_{10} i = b \log_{10}(i_o/i)$, where η_c is the overpotential (mV), i is the c.d. (A cm⁻²) and i_o is the exchange c.d. (A cm⁻²). Note that η will always be negative

Metal	Electrolyte	Temp. (°C)	$-\log_{10} i$ range	$-a$ (mV)	b (mV)	$-\log_{10} i_o$ (i_o in A cm ⁻²)
Ag	0.001 N HCl	20	6.0 to 2.0	810	125	6.5
	0.01 N HCl	20	6.0 to 2.0	820	130	6.3
	0.1 N HCl	20	6.0 to 3.3	570	90	6.3
	0.1 N HCl	20	3.3 to 1.0	670	120	5.6
	1.0 N HCl	20	6.0 to 2.3	320	60	5.4
	1.0 N HCl	20	2.3 to 1.0	480	130	3.7
	5.0 N HCl	20	6.0 to 2.8	470	70	6.7
	5.0 N HCl	20	2.8 to -2	630	120	5.3
	7.0 N HCl	20	6.0 to 3.4	640	90	7.1
Al	7.0 N HCl	20	3.4 to 1.0	740	110	6.7
	2 N H ₂ SO ₄	25	3.0 to 0.7	1000	100	10.0
Au	0.001 N HCl	20	7.0 to 2.0	524	72	7.32
	0.01 N HCl	20	6.0 to 2.0	558	84	6.63
	0.1 N HCl	20	6.6 to 3.0	468	71	6.59
	0.1 N HCl	20	3.0 to 2.0	548	97	5.64
	0.001 N NaOH	20	6.0 to 4.5	832	118	7.05
	0.01 N NaOH	20	6.5 to 3.7	836	119	7.04
	0.1 N NaOH	20	4.8 to 3.0	856	123	6.95
Be	1.0 N HCl	20	3.0 to 1.3	1080	120	9.0
Bi	1.0 N HCl	20	3.0 to 1.0	840	120	7.0
Cd	1.7 N H ₂ SO ₄	20	4.0 to 3.0	1450	120	12.1
	10 N H ₂ SO ₄	20	4.0 to 2.0	1400	120	11.7
Cu	0.001 N HCl	20	5.0 to 3.3	802	122	6.61
	0.01 N HCl	20	4.5 to 2.3	786	118	6.71
	0.1 N HCl	20	5.0 to 2.5	790	117	6.76
	0.005 N NaOH	16		890	139	6.40
	0.02 N NaOH	16	6.0 to 3.7	710	114	6.29
Fe	0.15 N NaOH	16		690	117	5.99
	0.001 N HCl	20	4.0 to 3.8	787	127	6.19
	0.01 N HCl	20	4.1 to 3.2	741	118	6.29
	1 N HCl	16	3.0 to 0.0	770	130	5.9
	0.01 N NaOH	20	4.5 to 3.8	776	117	6.62
	0.1 N NaOH	20	4.1 to 3.2	726	120	6.06
	4.8 N KOH	20	4.0 to 3.0	350	70	5.0
Ga	10.5 N KOH	20	4.0 to 3.0	340	70	4.9
	0.2 N H ₂ SO ₄	87		800	120	6.7
Hg	0.001-0.1 N HCl	20	7.0 to 1.0	1410	116	12.2
	1 N HCl	20	6.0 to 2.5	1390	119	11.7
	3 N HCl	20	6.0 to 2.5	1420	141	10.1
	5 N HCl	20	6.0 to 2.5	1320	127	10.4
	7 N HCl	20	6.0 to 2.5	1130	108	10.5
	10 N HCl	20	6.0 to 2.5	1020	95	10.7
	0.1 N H ₂ SO ₄	20	6.0 to 2.5	1440	114	12.7
	0.25 N H ₂ SO ₄	20	6.5 to 3.0	1403	116	12.1
	5 N H ₂ SO ₄	20	6.5 to 3.0	1400	116	12.05
	0.1 N LiOH	20	6.0 to 4.0	1598	102	15.7
	0.2 N LiOH	20	6.0 to 4.0	1545	100	15.5
	0.1 N NaOH	20	6.0 to 4.0	1457	100	14.6
	0.2 N NaOH	20	6.0 to 4.0	1405	97	14.5
Hg	0.002 N KOH	20	6.0 to 4.0	1682	98	17.1
	0.02 N KOH	20	6.0 to 4.0	1545	90	17.3
	0.1 N KOH	20	6.0 to 4.0	1430	93	15.4

*Data after Parsons, *Handbook of Electrochemical Constants*, Butterworths, London (1959).

Table 21.12 (continued)

<i>Metal</i>	<i>Electrolyte</i>	<i>Temp.</i> (°C)	$-\log_{10} i$ <i>range</i>	$-a$ (mV)	b (mV)	$-\log_{10} i_0$ (i_0 in A cm ⁻²)
Hg (cont.)	0.01 N Ba(OH) ₂	20	6.0 to 4.0	1170	45	26.0
	0.02 N Ba(OH) ₂	20	6.0 to 4.0	1220	65	18.8
	0.1 N DCl in D ₂ O	20	5.0 to 2.4	1485	119	12.19
Mo	0.001 N HCl	20	5.6 to 4.2	557	81	7.12
	0.01 N HCl	20	5.2 to 3.7	543	76	7.19
	0.1 N HCl	20	6.0 to 3.5	586	80	7.30
	0.1 N HCl	20	3.5 to 2.0	671	104	6.45
	0.001 N NaOH	20	5.9 to 4.4	667	92	7.27
	0.01 N NaOH	20	4.9 to 3.6	664	103	6.42
	0.1 N NaOH	20	4.7 to 3.7	641	87	7.35
	0.1 N NaOH	20	3.6 to 2.1	739	116	6.37
	1.0 N HCl	20	3.0 to 1.0	900	80	11.0
Ni	0.000 04 N HCl	20	6.0 to 5.0	650	100	6.5
	0.001 N HCl	20	5.8 to 3.3	617	93	6.6
	0.01 N HCl	20	5.5 to 3.3	611	91	6.7
	0.1 N HCl	20	5.0 to 2.0	626	104	6.0
	1.0 N HCl	20	4.3 to 2.0	594	109	5.4
	0.001 N NaOH	20	6.8 to 4.8	720	103	7.0
	0.006 N NaOH	20	6.3 to 3.8	660	101	6.6
	0.1 N NaOH	20	6.0 to 3.0	650	101	6.4
	0.1 N HCl	20	5.8 to 2.5	1524	116	13.2
Pb	1 N HCl	20	5.8 to 2.5	1531	119	12.9
	3 N HCl	20	5.1 to 2.5	1573	142	11.1
	5 N HCl	20	4.9 to 2.5	1495	140	10.7
	7 N HCl	20	4.7 to 2.5	1417	138	9.76
	10 N HCl	20	4.6 to 2.0	1195	135	8.84
	0.1 N H ₂ SO ₄	20	7.0 to 2.5	1533	118	13.0
	1 N H ₂ SO ₄	20	6.5 to 2.0	1536	119	12.9
	8 N H ₂ SO ₄	20	5.9 to 2.0	1530	120	12.8
	15 N H ₂ SO ₄	20	5.3 to 2.0	1469	121	12.1
	20 N H ₂ SO ₄	20	5.0 to 2.0	1411	119	11.9
	1 N HBr	20	5.3 to 2.3	1484	116	12.7
	3 N HBr	20	5.1 to 2.3	1467	123	11.9
	6 N HBr	20	4.7 to 2.3	1377	130	10.6
	8.5 N HBr	20	4.3 to 2.3	1285	140	9.17
	1 N HClO ₄	20	4.8 to 1.6	1537	118	13.0
	3 N HClO ₄	20	4.8 to 1.6	1517	118	12.8
	7 N HClO ₄	20	4.8 to 1.6	1504	121	12.4
	9 N HClO ₄	20	4.8 to 1.6	1453	122	11.9
	11.6 N HClO ₄	20	4.8 to 1.6	1446	132	11.0
	1.0 N H ₂ SO ₄	20	3.0 to 2.0	240	80	3.0
	0.01 N HCl	20	3.9 to 3.1	447	107	4.18
	0.1 N HCl	20	2.9 to 1.4	321	99	3.25
Pd	0.001 N NaOH	20	5.0 to 3.9	589	100	5.88
	0.01 N NaOH	20	5.4 to 4.0	610	110	5.56
	0.1 N NaOH	20	4.1 to 3.1	637	125	5.01
	0.5 N HCl	25	2.0 to 0.7	73	28	2.6
	0.01 N HCl	20	3.4 to 3.1	209	55	3.80
Rh	0.01 N NaOH	20	4.2 to 3.5	551	119	4.64
	2 N H ₂ SO ₄	20	3.0 to 0	900	100	9.0
Sb	1 N HCl	20	3.0 to 0	1100	140	8.0
Ta	1 N HCl	20	3.0 to 1.0	550	120	4.6
W	5 N HCl	20	2.0 to -2.0	550	110	5.0

Table 21.13 Exchange current densities i_0 for the hydrogen evolution reaction

<i>Metal</i>	$-\log i_0 [\text{A cm}^{-2}]$ in approx. 1 mol dm ⁻³ H ₂ SO ₄
Palladium	3.0
Platinum	3.1
Rhodium	3.6
Iridium	3.7
Nickel	5.2
Gold	5.4
Tungsten	5.9
Niobium	6.8
Titanium	8.2
Cadmium	10.8
Manganese	10.9
Thallium	11.0
Lead	12.0
Mercury	12.3

After Bockris, J. O'M. and Reddy, A. K. N., *Modern Electrochemistry*, Macdonald (1970).**Table 21.14** Exchange current densities and transfer coefficients α for evolution of gases at 20–25°C at different anodes

<i>Gas</i>	<i>Metal</i>	<i>Solution</i> ^a	α	i_0 (A cm ⁻²)
O ₂	Au	0.1 mol dm ⁻³ NaOH	0.74–1.2	5×10^{-13}
	Pt	0.5 mol dm ⁻³ H ₂ SO ₄	0.45	$10^{-8} - 10^{-11}$
	Pt	HNO ₃ + NaOH pH 0.5–14	0.51	$0.6 - 1 \times 10^{-10}$
	Pt	Phosphate buffer pH 6.8	0.29	
	Pt	0.1 mol dm ⁻³ NaOH	0.81	4×10^{-13}
	PbO ₂	0.5 mol dm ⁻³ H ₂ SO ₄	0.50	
Cl ₂		1.0 mol dm ⁻³ KOH	0.50	
	Pt	1.0 mol dm ⁻³ HCl	0.48	5×10^{-3}
	Pt	Various solutions	0.5–0.7	10^{-3}
	Ir	1.0 mol dm ⁻³	0.73	4×10^{-5}
	PbO ₂	0.5–2 mol dm ⁻³ NaCl	0.17–0.27	10^{-7}
	Br ₂	1 mol dm ⁻³ HBr	0.6	3×10^{-3}
N ₂	Pt	1 N KBr	0.5–0.7	3×10^{-3}
	Pt	1.0 mol dm ⁻³ NaN ₃	0.98	10^{-76}
	Ir	1.0 mol dm ⁻³ NaN ₃	1.0	10^{-75}
	Pd	1.0 mol dm ⁻³ NaN ₃	1.1	10^{-81}

Data after Parsons, *Handbook of Electrochemical Constants*, Butterworths, London (1959).

Table 21.15 Exchange current densities i_o at 25°C for some electrode reactions*

<i>Metal</i>	<i>System</i>	<i>Medium</i>	$-\log i_o$ (A cm ⁻²)
Mercury	Cr ³⁺ /Cr ²⁺	KCl	6.0
Platinum	Ce ⁴⁺ /Ce ³⁺	H ₂ SO ₄	4.4
Platinum	Fe ³⁺ /Fe ²⁺	H ₂ SO ₄	2.6
Rhodium	Fe ³⁺ /Fe ²⁺	H ₂ SO ₄	2.76
Iridium	Fe ³⁺ /Fe ²⁺	H ₂ SO ₄	2.8
Palladium	Fe ³⁺ /Fe ²⁺	H ₂ SO ₄	2.2
Gold	H ⁺ /H ₂	H ₂ SO ₄	3.6
Platinum	H ⁺ /H ₂	H ₂ SO ₄	3.1
Mercury	H ⁺ /H ₂	H ₂ SO ₄	12.1
Nickel	H ⁺ /H ₂	H ₂ SO ₄	5.2
Tungsten	H ⁺ /H ₂	H ₂ SO ₄	5.9
Lead	H ⁺ /H ₂	H ₂ SO ₄	11.3

*Data after Bockris, J. O'M. and Reddy, A. K. N., *Modern Electrochemistry*, Macdonald (1970).

Table 21.16 Exchange current densities for several noble metals and a platinum-rhodium alloy in the reduction of oxygen from perchloric acid solution*

<i>Metal or alloy</i>	<i>Exchange current density</i> i_o (A cm ⁻²)
Platinum	10 ⁻⁹
Platinum and 40 atomic % rhodium	10 ⁻⁹
Rhodium	6 × 10 ⁻⁹
Iridium	10 ⁻¹¹

*Data after Bockris, J. O'M. and Reddy, A. K. N., *Modern Electrochemistry*, Macdonald (1970).

Table 21.17 Exchange current densities for M^{n+}/M equilibria in different solutions*

<i>Metal</i>	<i>Solution</i>	i_o (A cm ⁻²)
Zn	Perchlorate	3 × 10 ⁻⁸
Pb	Perchlorate	8 × 10 ⁻⁴
Tl	Perchlorate	10 ⁻³
Ag	Perchlorate	1.0
Bi (amalgam)	Perchlorate	10 ⁻⁵
Ni	Sulphate	2 × 10 ⁻⁹
Fe	Sulphate	10 ⁻⁸ , 2 × 10 ⁻⁹
Zn	Sulphate	3 × 10 ⁻⁵
Cu	Sulphate	4 × 10 ⁻⁵ , 3 × 10 ⁻²
Tl	Sulphate	2 × 10 ⁻³
Sb	Chloride	2 × 10 ⁻⁵
Zn	Chloride	3 × 10 ⁻⁴ , 7 × 10 ⁻¹
Sn	Chloride	2 × 10 ⁻³
Bi	Chloride	3 × 10 ⁻²
Hg	Hg ₂ (NO ₃) ₂ + HClO ₄	2 × 10 ⁻¹

*Data after West, J. M., *Electrodeposition and Corrosion Processes*, 2nd edn, Van Nostrand Reinhold (1970).

Table 21.18 Structures, thermal data, and molar volumes of metal oxides and hydroxides, and of some double oxides*
A. Metal oxides and hydroxides

Compound	Remarks	Structure	m.p. etc. (°C)	b.p. etc. (°C)	$\Delta H_{\text{dec.}}$ (kJ)	Volume (cm ³)	σ^\dagger
Li ₂ O		CaF ₂	<i>sbl.</i>	s.p. 1300	1194·1	15·0	0·58
Li ₂ O ₂	α	<i>hexag.</i>	t.p. 225		77·5	21·45	0·83
	β		d. 160				
		Li ₂ O _{2-1.8}					
LiOH		SnO	m.p. 462	d. 770	137·3	16·4	1·26
Na ₂ O		CaF ₂		<i>d. vol.</i>	843·3	25·9	0·55
Na ₂ O ₂		<i>tetrag.</i>		d. 585	186·7	31·6	0·67
NaO ₃		NaCl(Cl=O ₂)			8·4	24·9	1·05
NaOH	α	<i>tetrag. B33</i>	t.p. 300		149·0	(18·8)	0·83
	β		m.p. 300	d. 1000	140·3		
K ₂ O		CaF ₂	d. vol.		723·5	40·4	0·45
K ₂ O ₂			m.p. 490	d.	173·3		
KO ₂	α	<i>tetrag.</i>	t.p. 80		117·2	33·0	0·73
	β	NaO ₂	m.p. 380	d.		34·0	0·75
KOH	α	<i>monocl.</i>	t.p. 249		205·2	26·5	0·58
	β	NaCl	m.p. 400	b.p. 1330	192·6	29·0	0·64
Rb ₂ O		CaF ₂		d.	660·7	46·4	0·42
Rb ₂ O ₂			m.p. 570	d. 920	192·6	55·6	0·50
Rb ₂ O ₃		Th ₃ P ₄	m.p. 489	d. 770	129·8	62·1	0·56
RbO ₂		CaC ₂	m.p. 412	d. 730	83·7	38·3	0·69
RbOH	α		t.p. 245		211·9	(32·0)	
	β	(NaCl)	m.p. 300		197·6		
Cs ₂ O			m.p. 4				
Cs ₄ O			d. 10				
Cs ₃ O		<i>hexag.</i>	m.p. 165			151·2	0·74
Cs ₂ O		CdCl ₂	m.p. 490	<i>d. vol.</i>	636·4	60·0	0·44
Cs ₂ O ₂			m.p. 594	d. 960	318·2		
Cs ₂ O ₃		Th ₃ P ₄	m.p. 502	d. 870	175·9	73·8	0·54

*Data after Kubaschewski and Hopkins, *The Oxidation of Metals and Alloys*, Butterworths, London (1962).

σ^\dagger is the ratio of the molar volume of the oxide expressed as MO_x or hydroxide as M(OH)_y to that of the pure metal.

Abbreviations are given on page 21.52

Table 21.18 (continued)

Compound	Remarks	Structure	m.p. etc. (°C)	b.p. etc. (°C)	$\Delta H_{\text{dec.}}$ (kJ)	Volume (cm ³)	ϕ
CsO ₂		CaC ₂	m.p. 432	d.	142.4		
CsOH	α		t.p. 223		253.3	(40.8)	
	β		m.p. 272				
BeO		wurtzite	m.p. 2530	b.p. 3850	1198.3	8.25	1.68
Be(OH) ₂	α		d. <250>		(55.3)	22.4	4.6
	β	c-Zn(OH) ₂			(58.6)	22.35	4.6
MgO		NaCl	sbl.	s.p. 2770	1203.3	11.25	0.81
MgO ₂	unst.		d. <50>				
Mg(OH) ₂		Cd(OH) ₂	d. 283		84.6	24.4	1.74
CaO		NaCl	m.p. 2600	b.p. (3500)	1268.7	16.7	0.64
CaO ₂	unst?	CaC ₂	d. <400>		50.2	22.4	
Ca(OH) ₂		Cd(OH) ₂	d. 550		118.9	33.2	1.28
SrO		NaCl	m.p. 2450		1180.7	20.4	0.61
SrO ₂		CaC ₂	d. 170		100.5	25.1/26.9	0.80
Sr(OH) ₂			d. 700		126.0		
BaO	BaO _{0.997-1.00}	NaCl	m.p. 1925	b.p. (2750)	1113.7	25.3	0.67
BaO ₂		CaC ₂	d. 720		163.3	29.9/31.2	0.82
Ba(OH) ₂			m.p. 408	d. 890	147.0		
Sc ₂ O ₃		cubic: D5 ₃			(1214.2)	35.4	1.19
ScOOH		γ -FeOOH				25.5	1.82
Sc(OH) ₃		cubic: ca. ReO ₃				36.5	2.4
Y ₂ O ₃		Sc ₂ O ₃	m.p. 2420	b.p. (4300)	1271.2	44.9	1.39
Y(OH) ₃		La(OH) ₃	d. <190>			36.6	2.27
La ₂ O ₃	A	hexag.: D5 ₂	m.p. 2320		1244.8	49.7	1.10
	C	Sc ₂ O ₃					
La(OH) ₃		hexag.: ca. Do19	d. 260		100.5	36.8/42.0	
Ce ₂ O ₃	A	A-La ₂ O ₃			(1277.0)	47.9	1.16
	B	Sc ₂ O ₃					
CeO ₂	unst.	CaF ₂	d. 2700		(523.4)	25.3	1.22
ThO	unst.?	NaCl				20.7/22.2	

Table 21.18 (continued)

Compound	Remarks	Structure	m.p. etc. (°C)	b.p. etc. (°C)	$\Delta H_{\text{dec.}}$ (kJ)	Volume (cm ³)	ρ
Th ₂ O ₃	<i>unst.</i>						
ThO ₂		CaF ₂	m.p. (3000)		1227.6	26.7	1.35
Th(OH) ₄	<i>unst.</i>	<i>amorph.</i>					
UO ₂	} > 1120°C complete sol. solns	CaF ₂	m.p. 2820		1084.4	24.7	1.98
U ₄ O ₉		<i>cubic</i>			351.7	97.0	1.94
U ₃ O ₈					305.6	100.4	2.77
UO ₃	UO ₂ ·6-2.67	<i>various</i>			233.6	(34.3)	
TiO	α TiO _{0.95-1.26}	NaCl, <i>dist.</i>	t.p. 990		1035.4		
	β TiO _{0.3-1.33}	NaCl	m.p. [1750]		1030.8	11.0/13.0	1.20
Ti ₂ O ₃	α	Cr ₂ O ₃	t.p. 200		963.8	31.5	1.46
	β		m.p. 1800		971.4		
Ti ₃ O ₅	α		t.p. 177				
	β	<i>orhomb.</i>			783.0	(52)	
Ti ₅ O ₉		<i>tricl.</i>				92.0	1.70
<i>rutile</i>	TiO _{1.91-2.0}	<i>tetrag.</i> : C4	m.p. 1920		737.7	18.8	1.73
<i>anatase</i>	915°C \uparrow <i>rutile</i>	<i>tetrag.</i>				19.3	1.78
<i>brookite</i>	<i>unst.</i>	<i>orhomb.</i>				19.8/20.5	1.89
ZrO ₂	α ZrO _{1.83-2.0}	<i>monocl.</i> : C43	t.p. 1170		1086.5	21.9	1.56
	β	<i>tetrag.</i>	m.p. 2700			20.2	1.45
VO	VO _{0.9-1.1}	NaCl	m.p. 1900		854.1	10.5/11.4	1.51
V ₂ O ₃		Cr ₂ O ₃			753.7	29.2/30.8	1.82
V ₃ O ₅							
VO ₂	α	<i>rutile</i>	t.p. 72		401.9	18.0	2.12
	β		m.p. [1360]		385.2		
V ₁₂ O ₂₆		<i>monocl.</i>	m.p. 670				2.60
V ₂ O ₅	VO ₂ ·495-2.50	<i>orhomb.</i> : D8 ₇	m.p. 674	d.*	251.2	54.0	3.19
Nb ₄ O	<i>unst.</i>	<i>tetrag. (interst.)</i>	d. (350)				
NbO	NbO _{0.93-1.0}	NaCl	m.p. 1945		(816.5)	15.0	1.37

*Decomposition begins below the m.p., proceeds gradually, and should be almost complete at 1700-1800°C when VO₂ is formed.

Table 21.18 (continued)

Compound		Remarks	Structure	m.p. etc. (°C)	b.p. etc. (°C)	$\Delta H_{\text{dec.}}$ (kJ)	Volume (cm ³)	ϕ
NbO ₂			ca. rutile	m.p. 1915		783.0	20.5	1.87
Nb ₂ O ₅	α	unst.	orthomb.					
	β	NbO _{2.43-2.50}	monocl.	m.p. 1495	d.†	614.6	58.3	2.68
Ta ₄ O		unst.	orthomb.				45.7	1.05
Ta ₂ O			tetrag. (interst.)					
TaO ₂		unst.	rutile					
Ta ₂ O ₃	α	TaO _{2.35-2.50}	orthomb.	t.p. 1350		819.0	54.0	2.50
	β		tricl.	m.p. 1872			52.8	2.43
Cr ₂ O ₃		CrO _{1.5-1.54}	rhombohed.: D5 ₁	m.p. 2400		753.7	29.0	2.07
CrO ₂		unst.?	rutile?			75.4		
CrO ₃		unst.	orthomb.	m.p. (187)		-6.3	35.6	5.1
MoO ₂		MoO _{1.97-2.08}	monocl.	dpr. 1780		588.7	19.7	2.10
Mo ₄ O ₁₁		MoO _{2.65-2.75}	orthomb.			311.5	134.0	3.57
Mo ₉ O ₂₆			monocl.	t.p. 650				3.5
Mo ₃ O ₂₃			monocl.					
MoO ₃		MoO _{2.95-3.00}	orthomb.	m.p. 795	b.p. 1100	324.9	31.3	3.3
WO ₂			MoO ₂	m.p. 1580	dpr.	589.9	19.8	2.08
W ₄ O ₁₁		WO _{2.65-2.72}	monocl.	dpr.			118.0	3.03
W ₂₀ O ₅₈		WO _{2.88-2.92}	monocl.	dpr.				3.12
WO ₃	α		tricl.	t.p. 735		561.5	31.5	3.35
	β		orthomb.	m.p. 1473				
WO ₃ H			ReO ₃				(52.5)	5.5
MnO		MnO _{1.0-1.12}	NaCl	m.p. 1875	d.	770.4	13.15	1.79
Mn ₃ O ₄	α	MnO _{1.33-1.45}	spinel, tetrag, def.	t.p. 1170		463.9	47.3	2.15
	β		cubic	m.p. 1560		422.0		
Mn ₂ O ₃	α	MnO _{1.5-1.6}	Sc ₂ O ₃	t.p. 600		212.7	(35.0)	
	γ		γ -Fe ₂ O ₃	d. 900				
MnO ₂	α	MnO _{1.96-2.0}	orthomb.	t.p. 250		160.8		
	β	unst.						
	γ		rutile	d. 480			16.6/17.2	2.27

†Decomposition to NbO₂ begins just above the m.p., but would not be complete below 2000°C.

Table 21.18 (continued)

Compound		Remarks	Structure	m.p. etc. (°C)	b.p. etc. (°C)	$\Delta H_{\text{dec.}}$ (kJ)	Volume (cm ³)	ρ
Mn ₂ O ₇		unst.				-207.3		
MnOOH	α		(FeS ₂)				20.2	2.75
	γ	manganite	monocl.: Eo6					
Mn(OH) ₂		pyrochroite	Cd(OH) ₂	d.		(38.1)	27.3	3.71
ReO ₂			MoO ₂			425.0		
ReO ₃			cubic: Do9	m.p. 160		372.6	31.5	3.38
Re ₂ O ₇			cubic: ca. c.p.	m.p. 296	b.p. 362	39.8	(79.2)	
FeO		FeO _{1.055-1.19}	NaCl	m.p. [1424]		529.7	11.9/12.5	
Fe ₃ O ₄			spinel	m.p. 1597		605.0	44.7	2.10
Fe ₂ O ₃	α	haematite	Cr ₂ O ₃	t.p. 675				
	β	unst.	β -Al ₂ O ₃			461.4	30.4	2.14
Fe ₂ O ₃	γ	unst.	cubic: D5 ₇	m.p. 1457		457.6		
	δ	unst.	hexag.					
FeOOH	α	goethite	orthomb: Eo2	d. (230)*		(75.4)*	21.3	3.0
	β	unst.	orthomb.				(27.5)	
	γ	lepidocrocite	orthomb: Eo4	d. (400)†		(102.6)	22.4	
Fe(OH) ₂			Cd(OH) ₂			54.4	26.4	3.7
Fe(OH) ₃		unst.	amorph.					
CoO		CoO _{1.0017}	NaCl	m.p. 1805		478.2	11.6/12.3	1.86
Co ₃ O ₄			spinel	d. 910			39.8	2.01
Co ₂ O ₃		unst.	hexag?				31.1/32.6	2.46
CoOOH		α, β, γ					20.6/22.2	
Co(OH) ₂			Cd(OH) ₂	d.		67.8	(25.0)	
NiO	n	NiO _{1.005}	NaCl	m.p. 1960	d.	481.5	10.9	1.65
	u	unst.	hexag?					
NiOOH	α		hexag.				26.3/28.6	4.33
	β	unst.	Cd(OH) ₂				19.9/22.1	
	γ		CdCl ₂				23.9	
Ni(OH) ₂	α		hexag.				24.3	
	β		Cd(OH) ₂			56.9	25.7	

*dt α -Fe₂O₃, †dt γ -Fe₂O₃.

Table 21.18 (continued)

Compound	Remarks	Structure	m.p. etc. (°C)	b.p. etc. (°C)	$\Delta H_{\text{dec.}}$ (kJ)	Volume (cm ³)	ρ
RuO ₂		<i>rutile</i>			439.6	(26.8)	
RuO ₄	<i>unst.</i>		m.p. 27		0.0	45.5	
RhO			d. 1020		181.7		
Rh ₂ O ₂		Cr ₂ O ₃	d. 990		208.5	31.3	1.88
PdO		<i>tetrag.</i> : B17	d. 790		182.1	14.7	1.65
Pd(OH) ₂			d. <100>				
OsO ₂		<i>rutile</i>	dpr.		257.5	28.2	3.24
OsO	<i>yellow</i>	<i>monocl.</i>	m.p. 56	b.p. 130	195.9	51.3/49.5	
IrO ₂		<i>rutile</i>	d. 1124		221.9	19.2	2.23
IrO ₃	<i>st.</i> : gas						
PtO	<i>unst.</i>	PdO					
Pt ₃ O ₄	<i>unst?</i>	b.c. <i>cubic</i>					
PtO ₂	<i>st.</i> : gas	<i>hexag.</i>					
Cu ₂ O		<i>cubic</i> : C3	m.p. 1230	<i>a.</i>	335.0	23.3	1.64
CuO		<i>monocl.</i> : B26	d. 1100		286.4	12.2	1.72
Cu(OH) ₂			d. 35		44.0	29.0	4.0
Ag ₂ O		Cu ₂ O	d. 185		61.1	32.1	1.56
AgO	<i>unst.</i>	<i>monocl.</i>					
ZnO		<i>wurtzite</i>	<i>d. vol.</i>		698.3	14.2	1.55
	<i>unst.</i>	<i>Zn blende</i>				14.5	1.59
Zn(OH) ₂	α	Cd(OH) ₂			61.1		
	β	<i>orthomb.</i> : C31	d. 80		51.5		
	γ	<i>orthomb.</i> : C31	d. 85		51.9		
	ϵ	<i>orthomb.</i>	d. 90		52.8		
CdO		NaCl	<i>d. vol.</i>		511.6	15.65	1.21
Cd(OH) ₂	CdO _{0.999-1.000} 2 modifications	<i>hexag.</i> : C6	d. 190		62.8	29.9	2.30
HgO	<i>red</i>	<i>orthomb.</i> : SnO, <i>def.</i>	d. 430		180.9	19.3	1.30
Al ₂ O	<i>st.</i> : gas						
AlO	<i>st.</i> : h.t.?		m.p. (2050)				

Table 21.18 (continued)

Compound		Remarks	Structure	m.p. etc. (°C)	b.p. etc. (°C)	$\Delta H_{\text{dec.}}$ (kJ)	Volume (cm ³)	ρ
Al ₂ O ₃	α	corundum	Cr ₂ O ₃	m.p. 2030		1117·1	25·6	1·28
	β	unst.	hexag.: H2 ₈				30·7	1·54
	γ	unst.	defect-spinel			1059·7	29·8	1·49
	δ		tetrag.					
	γ'	st.: electrolyt. layers	cubic					
AlOOH	χ	unst.	similar to γ					
	α	diaspore	α -FeOOH				17·8	1·78
γ	γ	böhmite	γ -FeOOH	d. (300)†		21·8†	19·5	1·95
	α	bayerite	amorph.			51·5†	30·9	3·09
Al(OH) ₃	γ	gibbsite	monocl.: Do7	d. (150)†		54·0†	32·0	3·20
						686·7	32·6	1·38
Ga ₂ O							29·1	1·23
Ga ₂ O ₃	α	unst.	Cr ₂ O ₃	m.p. 1725		734·8	31·6	1·35
	β		monocl.				37·7	
γ	γ	unst.	Sc ₂ O ₃					
GaOOH			α -FeOOH					
In ₂ O							35·1	1·12
In ₂ O ₃			Sc ₂ O ₃			620·9	39·3	1·26
In(OH) ₃		unst.	Sc(OH) ₃				37·5	2·4
Tl ₂ O				m.p. (300)		355·9	(44)	1·27
Tl ₂ O ₃			Sc ₂ O ₃	m.p. (715)	d.	175·8	45·2	1·31
TlO ₂				d. (490)				
TlOH				d. 140		57·8		
SiO		st.: gas	amorph.			(833·2)	(20·7?)	
Quartz	α	SiO ₂	hexag.: C8	t.p. 575		880·1	22·6	1·88
	β		hexag.	m.p. 1610		879·2	22·5	
Cristobalite	α	unst.	tetrag.: C30				25·8	2·15
	β		cubic: C9	m.p. 1713	d. vol.	876·3	27·0	

†dtr-Al₂O₃.

Table 21.18 (continued)

Compound		Remarks	Structure	m.p. etc. (°C)	b.p. etc. (°C)	$\Delta H_{\text{dev.}}$ (kJ)	Volume (cm ³)	ρ
Tridymite	α	unst.	orthomb.					
	β		hexag.: C10	t.p. 1470		875.5	26.5	
GeO			amorph.	s.p. 810			20.0	
GeO ₂	α		α -quartz	t.p. 1033		540.1	16.6	1.23
	β		rutile	m.p. 1116				
SnO		unst.	tetrag.: B10			572.8	(20.6)	
Sn ₃ O ₄				d. 1100				
SnO ₂	α		rutile	t.p. 410		580.7	21.5	1.32
	β			t.p. 540	d.			
Sn(OH) ₂						44.4		
Sn(OH) ₄						32.7		
Pb ₂ O		unst.	Cu ₂ O				47.0	1.29
PbO	α	red	SnO	t.p. 489		438.8	23.7	1.31
	β	yellow	orthomb.	m.p. 885	b.p. 1470	441.7	23.0	1.26
Pb ₃ O ₄		PbO _{1.33-1.57}	tetrag.	d. 550		154.1	(76)	1.4
Pb ₂ O ₃	α		monocl.			95.0	45.6/46.6	
	β	unst.?	orthomb.				49.6/50.4	
PbO ₂		PbO _{1.87-2.0}	rutile	d. 315		100.5	25.0	1.37
Pb(OH) ₂			hexag. c.p.			53.6	(31.8)	1.57
Sb ₂ O ₃	α	senarmontite	cubic: D6 ₁	t.p. 573		465.6	52.5/53.0	1.44
	β	valentinite	orthomb.: D5 ₁₁	m.p. 656	b.p. 1425	460.6	50.6	
SbO ₂	α		cubic: D6 ₂			209.3	(20.5)	
	β		orthomb.	d. (1080)				
Sb ₆ O ₁₃			cubic	d. 700				
Sb ₂ O ₅			cubic	d. (400)			77.9	2.12
Bi ₂ O ₃	α		monocl.: D5 ₅	t.p. 710		385.2	49.7	1.17
	β		tetrag.: D5 ₁₂	m.p. 817	b.p. 1890		50.9	1.20
	γ	unst.	cubic b.c.				51.8	1.22
		unst.	simple cubic				50.3	1.18

Table 21.18 (continued)
B. Some double oxides

Oxide		Remarks	Structure	m.p. etc. (°C)	Heat of decomp. (kJ)	Volume (cm ³)
Si, Ti, Zr						
Be ₂ SiO ₄		<i>phenakite</i>	<i>rhombohed.</i> : Si ₃	m.p. [1560]	(50·2)	37·1
MgSiO ₃	α	<i>enstatite</i>	<i>orthomb.</i>		36·4	(29·5)
	β	<i>unst.?: clinoenstat.</i>				
	γ	<i>st.</i> 1150°C		m.p. [1560]		
Mg ₂ SiO ₄		<i>forsterite</i>	<i>orthomb.</i> : Si ₂	m.p. 1890	63·2	43·7
CaSiO ₃	α	<i>wollastonite</i>	<i>monocl.</i> : Si ₃	m.p. 1540	90·0	39·5
Ca ₃ Si ₂ O ₇				m.p. [1460]		
Ca ₂ SiO ₄	α	<i>also denoted γ</i>	<i>orthomb.</i> : Hl ₂	t.p. 800	126·4	
	β	<i>also denoted α'</i>	<i>orthomb.</i>	t.p. 1430	122·3	52·1
	γ	<i>also denoted α</i>	<i>monocl. or hexag.</i>	m.p. 2130	118·9	54·2
Ca ₃ SiO ₃		<i>st.</i> 1250°C		d. 1900		
MgTi ₂ O ₃			Ti ₃ O ₃	m.p. 1660		
MgTiO ₃			Cr ₂ O ₃	m.p. [1640]		31·8
Mg ₂ TiO ₄			<i>spinel</i>	m.p. 1750	<i>sl. exo.</i>	44·7
CaTiO ₃	α	<i>perovskite</i>	E2 ₁ , <i>orthomb. def.</i>	t.p. 1260		33·6
	β			m.p. 1970		
Ca ₃ Ti ₂ O ₇				m.p. 1750		
CaZrO ₃			CaTiO ₃	m.p. 2400		38·5
ZrSiO ₄		<i>zircon</i>	<i>tetrag.</i> : HO ₃	m.p. 2430		39·0
MnSiO ₃		<i>rhodonite</i>	<i>tricl.</i>	m.p. [1270]	24·7	
Mn ₂ SiO ₄		<i>tephroite</i>	Mg ₂ SiO ₄	m.p. [1340]	49·4	46·7
MnTiO ₃		<i>pyrophanite</i>	Cr ₂ O ₃	m.p. [1360]		33·3
Mn ₂ TiO ₄			<i>spinel</i>	m.p. 1450		49·1
Fe ₂ SiO ₄		<i>fayalite</i>	Mg ₂ SiO ₄	m.p. 1205	35·2	47·6
Co ₂ SiO ₄			Mg ₂ SiO ₄	m.p. 1420		45·3

Table 21.18 (continued)

Oxide	Remarks	Structure	m.p. etc. (°C)	Heat of decomp. (kJ)	Volume (cm ³)
FeTi ₂ O ₃					55.3
FeTi ₂ O ₄		<i>spinel</i>			45.6
FeTiO ₃	<i>ilmenite</i>	Cr ₂ O ₃	m.p. 1370	(16.7)	31.7
Fe ₂ TiO ₃	<i>pseudobrookite</i>	Ti ₃ O ₅			54.8
CoTiO ₃		Cr ₂ O ₃			
Co ₂ TiO ₄		<i>spinel</i>		8.4*	44.9
Zn ₂ SiO ₄	<i>willemite</i>	Be ₂ SiO ₄	m.p. 1510	29.3	52.9
Zn ₂ TiO ₄		<i>spinel</i>	m.p. 1550	<i>sl. exo.</i>	45.9
Al ₂ SiO ₅	<i>kyanite</i>	<i>tricl.</i>		166.2	(45.0)
	<i>andalusite</i>	<i>orthomb.</i>		164.5	(50.5)
	<i>sillimanite</i>	<i>orthomb.</i>	m.p. [1810]	192.6	50.0
	<i>mullite</i>	<i>orthomb.</i>	m.p. 1920		118.3
Al ₆ Si ₂ O ₁₈		Ti ₃ O ₅	t.p. 1820		49.4
Al ₂ TiO ₅	α		m.p. 1890		
	β	<i>monocl.</i>	m.p. 765	10.5	45.2
PbSiO ₃			m.p. 743	29.3	
Pb ₂ SiO ₄			t.p. 137		
Pb ₄ SiO ₆	α		t.p. 720		
	β		m.p. 727		
	γ		t.p. 490	<i>sl. exo.</i>	38.5
PbTiO ₃	α	CaTiO ₃ , <i>def.</i>	m.p. 1170		
	β				
PbZrO ₃		<i>tetrag. ca. E2₁</i>			42.4
Al					
BeAl ₆ O ₁₀			m.p. 1910		
BeAl ₂ O ₄	<i>chrysoberyl</i>	<i>orthomb.</i>	m.p. 1870		34.0
MgAl ₂ O ₄	<i>spinel</i>	<i>cable: Hl₁</i>	m.p. 2135		39.7

*Free-energy values at 1000°C approximately equal to the heats of decomposition, assuming that $\Delta S \approx 0$.

Table 21.18 (continued)

Oxide	Remarks	Structure	m.p. etc. (°C)	Heat of decomp. (kJ)	Volume (cm ³)
Ca ₃ Al ₆ O ₁₄	<i>hercynite</i>	<i>cubic: K7₄</i>	m.p. 1455	15·5	218·0
CaAl ₂ O ₄			m.p. 1600		
Ca ₃ Al ₂ O ₆		<i>cubic</i>	m.p. [1535]		
LaAlO ₃		<i>CaTiO₃</i>		6·7	32·5
NbAlO ₄			m.p. 1510		
MnAl ₂ O ₄		<i>spinel</i>	m.p. [1560]		
FeAl ₂ O ₄		<i>spinel</i>	m.p. 1440	20·5*	42·5
Fe ₂ Al ₂ O ₆			d. 1230		
CoAl ₂ O ₄		<i>spinel</i>	m.p. 1960		
NiAl ₂ O ₄		<i>spinel</i>	m.p. 2020	21·8*	39·4
CuAlO ₂				8·4*	39·1
CuAl ₂ O ₄					39·5
ZnAl ₂ O ₄		<i>spinel</i>	m.p. (1950)		39·7
V, Nb, Ta					
Mg ₂ VO ₄	<i>α</i> <i>β</i>	<i>spinel</i>			44·7
MgV ₂ O ₄		<i>spinel</i>			44·85
BeNb ₈ O ₂₁			m.p. 1365		
BeNb ₆ O ₁₆			m.p. 1365		
BeNb ₄ O ₁₁			m.p. 1445		
BeNb ₂ O ₆			m.p. 1445		
MgNb ₂ O ₆		<i>columbite</i>			58·8
		<i>rutile</i>	m.p. 1480		62·1
Mg ₄ Nb ₂ O ₉		<i>haematite</i>			
Ca ₃ Nb ₂ O ₈		<i>Na_xWO₃ (x < 1)</i>			
Ca ₄ Nb ₂ O ₉		<i>tetrag.: perovskite</i>			113·6
TiNb ₂ O ₇			m.p. 1490		

*Free-energy values at 1000°C approximately equal to the heats of decomposition, assuming that $\Delta S \approx 0$.

Table 21.18 (continued)

Oxide	Remarks	Structure	m.p. etc. (°C)	Heat of decomp. (kJ)	Volume (cm ³)
CrNbO ₄		<i>rutile</i>			39.35
FeV ₂ O ₄		<i>spinel</i>			45.6
FeNbO ₄	α	<i>columbite</i>			76.1
	β	<i>rutile</i>			83.2
FeTa ₂ O ₆		<i>tetrag.</i>			62.8
Co ₂ Nb ₄ O ₁₄	α	<i>columbite</i>			101.7
	β	<i>rutile</i>			103.3
NiNb ₂ O ₆	α	<i>columbite</i>			55.2
	β	<i>rutile</i>			61.0
Zn ₃ VO ₄		<i>spinel</i>			
ZnV ₂ O ₄		<i>spinel</i>			45.0
ZnNb ₂ O ₆		<i>columbite</i>			
ZnNbO ₃			m.p. 1150		
UTa ₂ O ₈		U ₃ O ₈			
UTa ₂ O ₇		<i>cubic f.c.</i>			
<hr/>					
Cr, Mo, W					
MgCr ₂ O ₄		<i>spinel</i>	m.p. 2200	20.9	43.3
CaMoO ₄	<i>powellite</i>	CaWO ₄			46.7
MgWO ₄		<i>monocl.</i>		(14.2)	48.0
CaWO ₄	<i>scheelite</i>	<i>tetrag.</i> : HO ₄		(166.6)	47.5
CeCrO ₃		CaTiO ₃	m.p. 2430		
LaCrO ₃		CaTiO ₃			35.2
MnCr ₂ O ₄		<i>spinel</i>			46.0
FeCr ₂ O ₄	<i>chromite</i>	<i>spinel</i>	m.p. 2180	34.3*	44.0
CoCr ₂ O ₄		<i>spinel</i>			43.3
NiCr ₂ O ₄		<i>spinel</i>		8.4*	43.0

*Free-energy values at 1000°C approximately equal to the heats of decomposition, assuming that ΔS=0.

Table 21.18 (continued)

Oxide	Remarks	Structure	m.p. etc. (°C)	Heat of decomp. (kJ)	Volume (cm ³)
FeWO ₄	<i>ferberite</i>	MgWO ₄		(40.2)	(42.7)
NiWO ₄		MgWO ₄			
CuCr ₂ O ₄	<i>wulfenite</i>	CuFe ₂ O ₄			43.8
ZnCr ₂ O ₄		<i>spinel</i>			43.3
PbMoO ₄		CaWO ₄	m.p. 1065	(138.6)	52.8
Pb ₂ MoO ₅			m.p. 950		
PbWO ₄	α	CaWO ₄	t.p. 870	(110.9)	(56.0)
	β	<i>monocl.</i>	m.p. 1120		
Pb ₂ WO ₅			m.p. 900		
LaMnO ₃		CaTiO ₃			35.2
FeMnO ₃					31.9
Fe ₂ MnO ₄		<i>spinel</i>			46.0
CuMn ₂ O ₄					47.4
ZnMn ₂ O ₄		<i>tetrag.</i> : Mn ₃ O ₄			45.9
<hr/>					
Fe, Co, Ni					
MgFe ₂ O ₄		<i>spinel</i>	m.p. [1750]	18.8*	44.3
MgCo ₂ O ₄		<i>spinel</i>			40.1
CaFe ₂ O ₄		V ₂ CaO ₄	m.p. [1240]		
Ca ₂ Fe ₂ O ₅			m.p. [1480]	31.0	
LaFeO ₃		CaTiO ₃	m.p. 1890		35.5
Fe ₂ CoO ₄	<i>trf.</i> 500°C	<i>spinel</i>			44.6
Fe ₂ NiO ₄	<i>trf.</i> 582°C	<i>spinel</i>			44.8
Co ₂ NiO ₄		<i>spinel</i>			40.2
CuFe ₂ O ₄		<i>spinel, tetrag. def.</i>	m.p. [900]		45.3
CuFeO ₂		NaHF ₂			27.5
CuCo ₂ O ₄		<i>spinel</i>			39.1

*Free-energy values at 1000°C approximately equal to the heats of decomposition, assuming that ΔS = 0.

Table 21.18 (continued)

<i>Oxide</i>	<i>Remarks</i>	<i>Structure</i>	<i>m.p. etc.</i> (°C)	<i>Heat of decomp.</i> (kJ)	<i>Volume</i> (cm ³)
ZnFe ₂ O ₄		<i>spinel</i>	m.p. 1720	<i>exo.</i>	45.2
GeNi ₂ O ₄		<i>spinel</i>			41.5
SnCo ₂ O ₄		<i>spinel</i>			47.9
PbFe ₄ O ₇		<i>hexag.</i>			82.8
<hr/>					
Others					
Mg ₂ SnO ₄		<i>spinel</i>			47.5
CaSnO ₃		CaTiO ₃			36.8
MgLa ₂ O ₄			m.p. 2030		
CaCeO ₃		CaTiO ₃			34.4
CaUO ₃		Se ₂ O ₃	m.p. [1850]		
CaUO ₄	Ca(UO ₂)O ₂	<i>rhombohed.</i>			46.0
Ca ₂ UO ₄		<i>tetrag.</i>	m.p. [1800]		
Zn ₂ SnO ₄		<i>spinel</i>			48.0
PbSnO ₃		CaTiO ₃ , <i>def.</i>			

Abbreviations: amorph., amorphous; b.p., boiling point; b.c., body centred; c.p., close packed; d., dissociation temperature calculated; d.(.), dissociation temperature observed; *dpr.*, disproportionation; *def.*, distorted, deformed; d.vol., dissociation, forming gaseous dissociation products; endo., endothermic; exo., exothermic; f., form; f.c., face centred; hexag., hexagonal; h.t., at high temperature; h.t.f., high temperature form; l.t., at low temperature; l.t.f., low temperature form; m.p., melting point; m.[], melting associated with decomposition; m) †, melting point under pressure; max., maximum solubility; monocl., monoclinic; orthomb., orthorhombic; ppt. precipitated; qu., quartz; r.t., room temperature; rhombohed., rhombohedral; sl.exo., slightly exothermic; *s.sbl.*, sublimation point; vol., solid; st., stable; sur.lay., surface layer; tetrag., tetragonal; tricl., triclinic; unst., unstable; v.small, very small (solubility); †, converted into; () inaccurate or unreliable data.

Table 21.19 Solubility of gases in water

		<i>Temperature of water ($\theta/^{\circ}\text{C}$)</i>							
		0	10	15	20	30	40	50	60
Ammonia	S	1130	870	770	680	530	400	290	200
Argon	A	0.054	0.041	0.035	0.032	0.028	0.025	0.024	0.023
Carbon dioxide	A	1.676	1.163	0.988	0.848	0.652	0.518	0.424	0.360
Carbon monoxide	A	0.035	0.028	0.025	0.023	0.020	0.018	0.016	0.015
Chlorine	S	4.61	3.09	2.63	2.26	1.77	1.41	1.20	1.01
Helium	A	0.0098	0.0091	0.0089	0.0086	0.0084	0.0084	0.0086	0.0090
Hydrogen	A	0.0214	0.0195	0.0188	0.0182	0.0170	0.0164	0.0161	0.0160
Hydrogen sulphide	A	4.53	3.28	2.86	2.51	1.97	1.62	1.37	1.18
Hydrochloric acid	S	512	475	458	442	412	385	362	339
Nitrogen	A	0.0230	0.0183	0.0165	0.0152	0.0133	0.0119	0.0108	0.0100
Nitrous oxide	A	—	0.88	0.74	0.63	—	—	—	—
Nitric oxide	A	0.071	0.055	0.049	0.046	0.039	0.034	0.031	0.029
Oxygen	A	0.047	0.037	0.033	0.030	0.026	0.022	0.020	0.019
Sulphur oxide	S	79.8	56.6	47.3	39.4	27.2	18.8	—	—

Values of A for 20°C for other rare gases are: Ne, 0.0101; Kr, 0.0594; Xe, 0.126. S indicates the number of m^3 of gas measured at 0°C and $101.325 \text{ kN m}^{-2}$ which dissolve in 1 m^3 of water at the temperature stated, and when the pressure of the gas plus that of the water vapour is $101.325 \text{ kN m}^{-2}$. A indicates the same quantity except that the gas itself is at the uniform pressure of $101.325 \text{ kN m}^{-2}$ when in equilibrium with water.

Table 21.20A Solubility of air in water*

A kilogram of water saturated with air at a pressure of $101.325 \text{ kN m}^{-2}$ contains the following volumes of dissolved oxygen, etc., in cm^3 at 0°C and $101.325 \text{ kN m}^{-2}$

<i>Gas</i>	<i>Temperature of water ($\theta/^{\circ}\text{C}$)</i>						
	0	5	10	15	20	25	30
Oxygen	10.19	8.9	7.9	7.0	6.4	5.8	5.3
Nitrogen, argon, etc.	19.0	16.8	15.0	13.5	12.3	11.3	10.4
Sum of above	29.2	25.7	22.9	20.5	18.7	17.1	15.7
% of oxygen in dissolved air (by vol.)	34.9	34.7	34.5	34.2	34.0	33.8	33.6

*After Kaye, G. W. C. and Laby, T. H., *Tables of Physical and Chemical Constants*, 14th ed., Longmans (1973).

Table 21.20B Solubility of oxygen in certain electrolyte solutions*

<i>Electrolyte</i>	<i>Conc. of electrolyte (mol/l)</i>			
	0.5	1.0	2.0	
				<i>Solubility (ml/l)†</i>
HNO_3	27.67	27.03	26.03	25°C
HCl	27.13	26.30	24.47	
H_2SO_4	25.20	23.00	19.15	
NaCl	24.01	20.44	14.48	
KOH	23.09	18.88	—	
NaOH	22.91	18.69	12.19	
HNO_3	33.00	31.86	29.87	15°C
HCl	32.62	31.01	28.35	
H_2SO_4	32.05	31.76	22.09	
NaCl	29.20	24.65	17.26	
KOH	27.59	22.19	—	
NaOH	27.31	21.90	14.41	

*Data after Uhlig, H. H. (Ed.), *Corrosion Handbook*, Wiley (1953).

†Solubility given in cubic centimetres of gas ($^{\circ}\text{C}$, 1 atm) dissolved in 1 litre of solution when partial pressure of the gas equals one atmosphere.

Table 21.21 Oxygen dissolved in sea-water in equilibrium with a normal atmosphere ($101\,325\text{ N m}^{-2}$) of air saturated with water vapour*

<i>Parts per million</i>					
Chlorinity ‰	0	5	10	15	20
Salinity ‰	0	9.06	18.08	27.11	36.11
<i>Temperature ($^{\circ}\text{C}$)</i>					
0	14.62†	13.70	12.78	11.89	11.00
5	12.79	12.02	11.24	10.49	9.74
10	11.32	10.66	10.01	9.37	8.72
15	10.16	9.67	9.02	8.46	7.92
20	9.19	8.70	8.21	7.77	7.23
25	8.39	7.93	7.48	7.04	6.57
30	7.67	7.25	6.80	6.41	5.97

Note: the table gives the quantity of oxygen dissolved in sea-water at different temperatures and chlorinities when in equilibrium with a normal atmosphere saturated with water vapour. It thus represents the condition approached by the surface water when biological activity is not excessive.

*Data after C. J. J. Fox, Conseil Permanent International pour l'Exploration de la Mer, Copenhagen, *Publication de Ciconstance*, 41 (1907).

†The values of solubility in water of zero chlorinity differ slightly from those for fresh water.

Table 21.22 Saturated solubilities of atmospheric gases in sea-water at various temperatures*
Concentrations of oxygen, nitrogen and carbon dioxide in equilibrium with 1 atm ($101\,325\text{ N m}^{-2}$) of designated gas

<i>Gas</i>	<i>Chlorinity</i> (‰)	<i>Temperature</i> ($^{\circ}\text{C}$)	<i>Concentration</i>	
			ml/l	<i>Parts per million</i>
Oxygen	0	0	49.2†	70.4
		12	36.8	52.5
		24	29.4	42.1
	16	0	40.1	56.0
		12	30.6	42.9
		24	24.8	34.8
	20	0	38.0	52.8
		12	29.1	40.4
		24	23.6	32.9
Nitrogen	0	0	23.0†	28.8
		12	17.8	22.7
		24	14.6	18.3
	16	0	15.0	18.4
		12	11.6	14.2
		24	9.36	11.5
	20	0	14.2	17.3
		12	11.0	13.4
		24	8.96	10.9

Table 21.22 (continued)

Gas	Chlorinity (‰)	Temperature (°C)	Concentration	
			ml/l	Parts per million
Carbon dioxide†	0	0	1715†	3370
		12	1118	2198
		24	782	1541
	16	0	1489	2860
		12	980	1888
		24	695	1342
	20	0	1438	2746
		12	947	1814
		24	677	1299

* Calculated from data in Sverdrup, H. U., Johnson, M. W., and Fleming, R. H., *The Oceans*, Prentice-Hall, Inc., New York (1942).

† These values differ slightly from those for fresh water.

‡ Includes CO₂ present as H₂CO₃ but not as HCO₃⁻ or CO₃²⁻.

Note: atmospheric gases are present in sea-water in approximately the following quantities:

	ml/l	Parts per million
Oxygen	0-9	0-12
Nitrogen	8-15	10-18
Carbon dioxide*	33-56	64-107
Argon	0.2-0.4	0.4-0.7
Helium and neon	1.7×10^{-4}	0.3×10^{-4} †

* Includes CO₂ present as H₂CO₃, HCO₃⁻ and CO₃²⁻

† Estimated as helium.

Table 21.23 Properties of sea-water of different salinities*

Salinity (‰)	Freezing point (°C)	Temperature of maximum density	Osmotic pressure (atm)	Specific heat (J kg ⁻¹)
0	0.00	3.95	0	4.184×10^3
5	-0.27	2.93	3.23	4.109×10^3
10	-0.53	1.86	6.44	4.050×10^3
15	-0.80	0.77	9.69	4.008×10^3
20	-1.07	-0.31	12.98	3.979×10^3
25	-1.35	-1.40	16.32	3.954×10^3
30	-1.63	-2.47	19.67	3.929×10^3
35	-1.91	-3.52	23.12	3.899×10^3
40	-2.20	-4.54	26.59	3.874×10^3

* Data after Subow, N. N., *Oceanographical Tables*, p. 208, Moscow (1931). Thompson, T. G., 'The Physical Properties of Sea Water', *Bull. 85*, 'Physics of the Earth. V. Oceanography', p. 63, National Research Council of the National Academy of Sciences, Washington (1932).

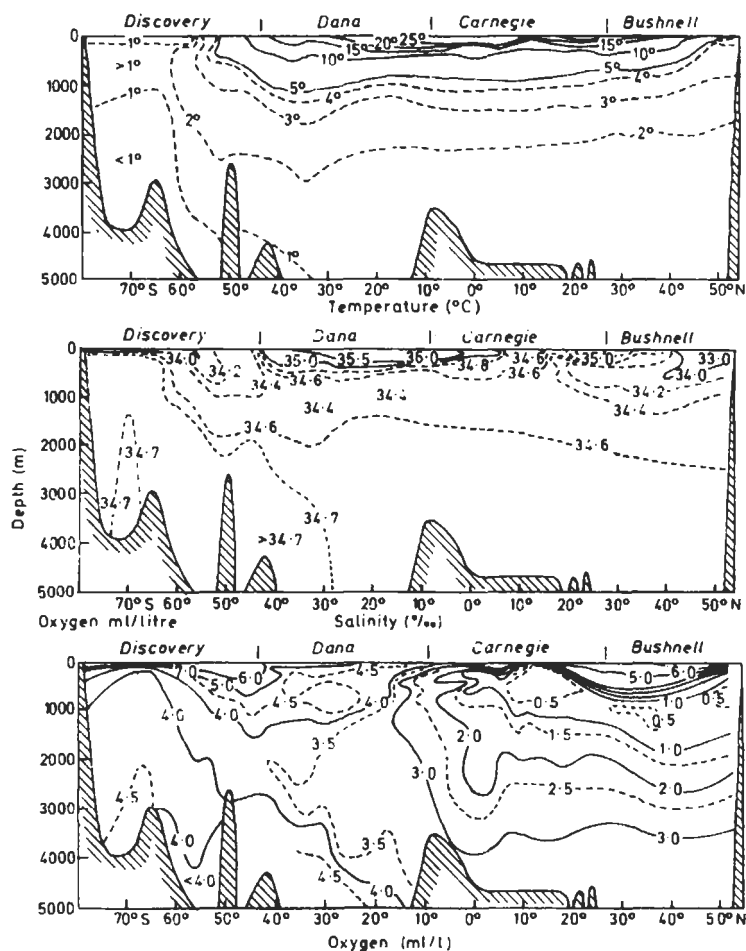


Fig. 21.3 Vertical sections showing distribution of temperature, salinity, and oxygen in the Pacific Ocean, approximately along the meridian of 170°W. (After Sverdrup, H. U., *Oceanography for Meteorologists*, Allen and Unwin (1945))

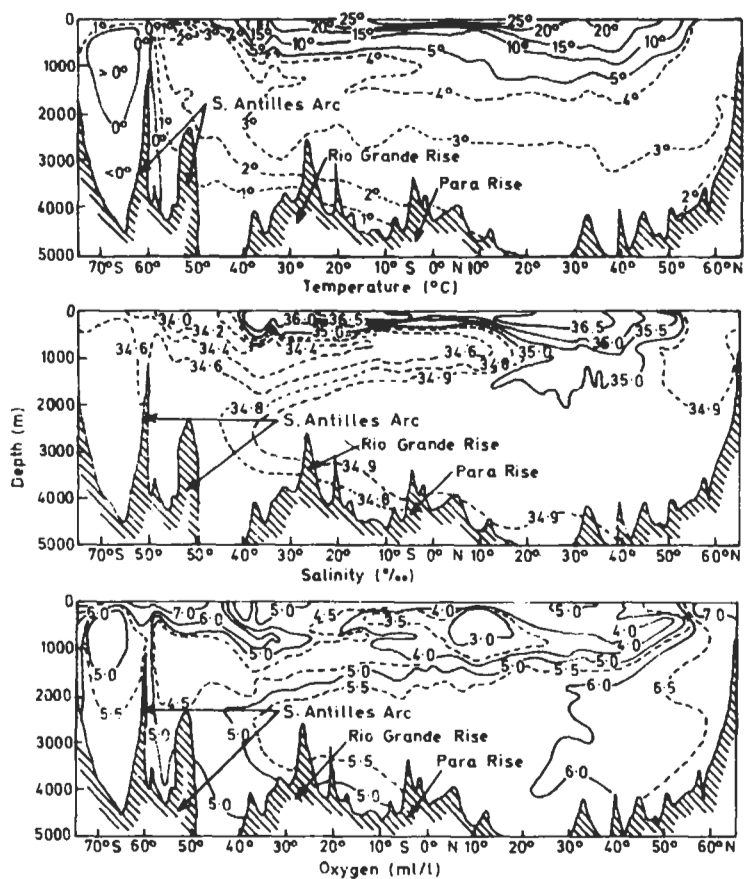


Fig. 21.4 Vertical sections showing distribution of temperature, salinity, and oxygen in the Western Atlantic Ocean (After Wüst). (After Sverdrup, H. U., *Oceanography for Meteorologists*, Allen and Unwin (1945))

Table 21.24 Resistivity of waters (approximate values Ω cm)*

Pure water	20 000 000
Distilled water	500 000
Rain water	20 000
Tap water	1-5000
River water (brackish)	200
Sea-water (coastal)	30
Open sea	20-25

*Data after Morgan, J. H., *Cathodic Protection*, Leonard Hill, London (1959).

Note: the resistivity of sea-water drops as the chlorinity and temperature rise and in open sea-water (chlorinity 19‰) it varies from about 16 Ω cm in the tropics to 35 Ω cm in the Arctic.

Table 21.25 Soil resistivities and corrosiveness

<i>Range of resistivity (Ω cm)*</i>	<i>Location</i>	<i>Soil type and classification</i>
10 000-100 000 and above	Perth, Scotland	Comparatively non-corrosive. Red sandstone
8000-10 000	West Durham	Mildly corrosive. Sandstone and shale
Varying 1000-20 000	Staffordshire	Many built-up areas. Possibly very corrosive
1000-1500	Eastbourne, Sussex	Marshy ground. Very corrosive
15 000-20 000	Sussex Downs	Chalk. Non-corrosive
750-1500	Port Clarence, S.E. Durham	Salt marsh. Very corrosive
600-1500	S. Essex	Essex clay. Very corrosive
1400-3200	Newport, Gwent	Grey, yellow and blue clays. Corrosive
12 000-15 000	North Devon	Millstone grit. Comparatively non-corrosive
1000-2500	Gloucester	Generally clay. Corrosive
25 000-250 000	West Hampshire	Sandy gravel. Not generally corrosive

*To obtain Ω m divide by 100.

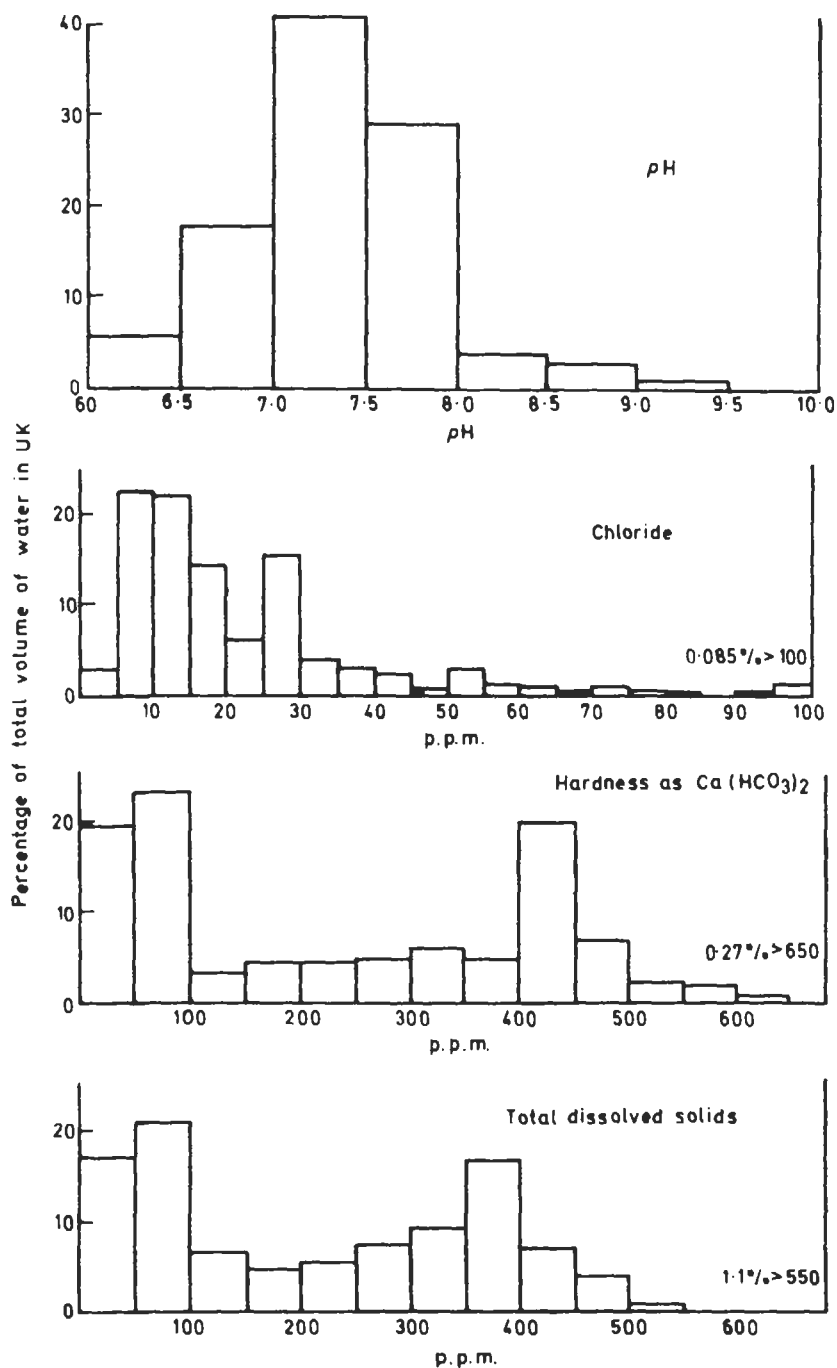


Fig. 21.5 Distribution of dissolved constituents in UK fresh waters. (After Butler, G. and Ison, H. C. K., *Corrosion and its Prevention in Water*, Leonard Hill, London (1966))

Table 21.26 Compositions of natural waters arranged in increasing chloride concentration (concentration in p.p.m.)

Type	Source	Total dissolved solids	Cl ⁻	SO ₄ ²⁻	Ca ²⁺	Mg ²⁺	Alkalinity (CaCO ₃)	pH	Hardness (CaCO ₃)		Free CO ₂
									Total	Temporary	
Reservoir	Vaich Res., Scot.	37	Trace	17	3	<1	—	6.2	—	—	—
Bay	Shawinigan Falls, Quebec	34	2	0	—	—	—	6.8	15	—	—
Lake	Lake Vyrnwy, Wales	40	7	5	—	—	8	7.0	16	—	3
Mains	Bristol	283	14	31	105	10	—	7.6	210	154	5
Mains	Teddington	360	51	32	118	20	200	7.5-8.0	320	240	5
Mains	Kuwait	336	108	48	37	10	—	9.3	—	—	—
Deep well	Reading	511	117	39	42	29	—	—	233	216	(+ HCO ₃) 152
Borehole	New Windsor	870	215	—	—	—	265	7.7	195	195	7
Artesian well	New Windsor	1250	320	—	—	—	271	—	700	150	—
Mains	Bledington, Oxon.	2968	540	1080	35	12	—	8.1	165	165	—
Mains	Benghazi	—	540	112	82	64	210	7.8	470	120	—
Mains	Aden	1860	582	423	103	113	160	7.8	715	160	4
Mains	Malta	1525	681	65	142	37	—	—	393	—	—
Well	Damman, Saudi Arabia	2656	1 041	489	241	89	—	—	—	—	—
Borehole	Harwich	2577	1 132	136	—	—	—	7.8	602	305	—
Well	Awali, Bahrain	15 000	7 310	561	688	309	160	7.1	2990	—	—
Sea	Average figure	34 800	19 500	2380	380	1250	—	8.2	—	—	—

Data after Butler, G. and Ison, H. C. K., *Corrosion and its Prevention in Water*, Leonard Hill, London (1966).

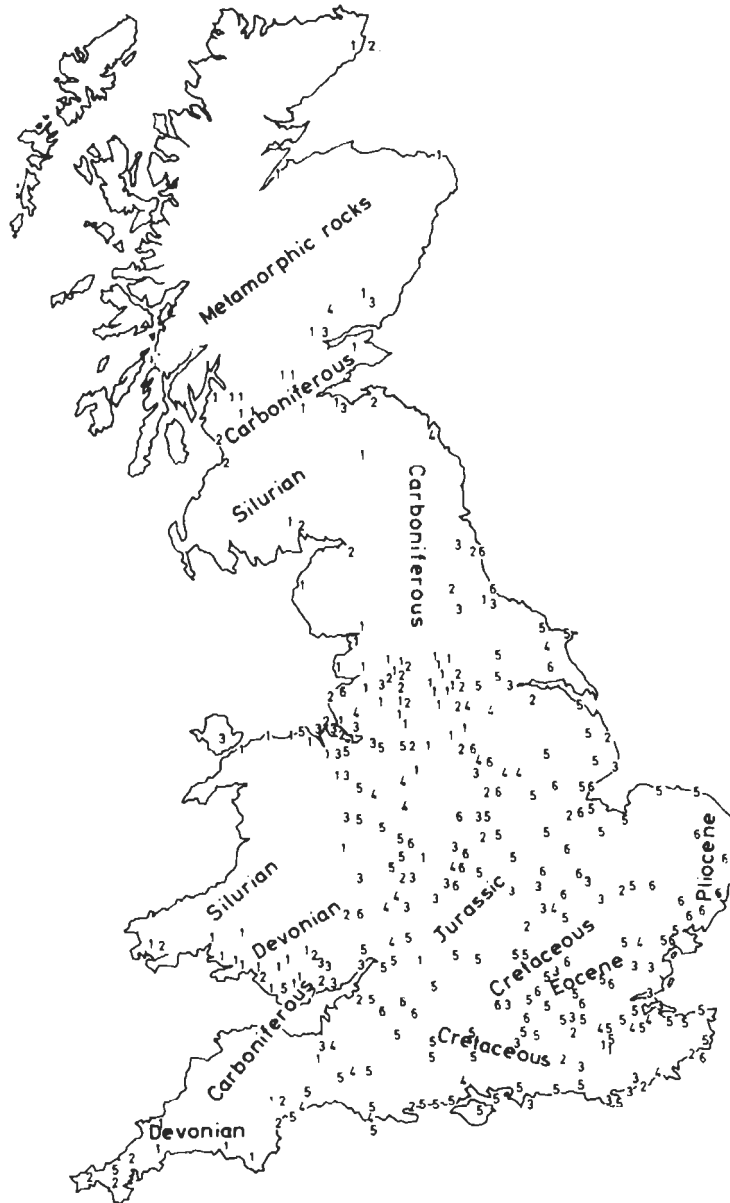


Fig. 21.6 Variation of hardness of water in England, Scotland and Wales in relation to geological formations. (After Butler, G. and Ison, H. C. K., *Corrosion and its Prevention in Water*, Leonard Hill, London (1966))

- | | |
|------------------------------------|-------------------------------------|
| 1. Up to 50 p.p.m. — very soft | 4. 150–200 p.p.m. — moderately hard |
| 2. 50–100 p.p.m. — moderately soft | 5. 200–300 p.p.m. — hard |
| 3. 100–150 p.p.m. — slightly hard | 6. Over 300 p.p.m. — very hard |

Table 21.27 Corrosion-rate conversion factors

<i>Multiply</i>	<i>by</i>	<i>To obtain</i>
Milligrams per square decimetre per day ($\text{mg dm}^{-2} \text{d}^{-1}$ or mdd)	10	grams per square metre per day ($\text{g m}^{-2} \text{d}^{-1}$ or gmd)
Inches per year (in y^{-1} or ipy)	25.4	millimetres per year (mm y^{-1} or mpy)
Milligrams per square decimetre per day (mdd)	$0.00144/\rho$ (ρ in g cm^{-3})	inches per year (ipy)
Milligrams per square decimetre per day (mdd)	$0.03652/\rho$ (ρ in g cm^{-3})	millimetres per year (mpy)
Grams per square metre per day (gmd)	$0.36525/\rho$ (ρ in g cm^{-3})	millimetres per year (mpy)
Grams per square inch per hour	372 000	milligrams per square decimetre per day ($\text{mg dm}^{-2} \text{d}^{-1}$)
Grams per square metre per year	0.0274	milligrams per square decimetre per day ($\text{mg dm}^{-2} \text{d}^{-1}$)
Milligrams per square decimetre	0.000 327 7	ounces per square foot (oz ft^{-2})
Milligrams per square decimetre per day	0.000 002 69	grams per square inch per hour ($\text{g in}^{-2} \text{h}^{-1}$)
Milligrams per square decimetre per day	36.5	grams per square metre per year ($\text{g m}^{-2} \text{y}^{-1}$)
Milligrams per square decimetre per day	0.007 48	pounds per square foot per year ($\text{lb ft}^{-2} \text{y}^{-1}$)
Ounces per square foot	3052	milligrams per square decimetre (mg dm^{-2})
Pounds per square foot per year	133.8	milligrams per square decimetre per day ($\text{mg dm}^{-2} \text{d}^{-1}$)
Grams per square metre per day	$0.36525/\rho$ (ρ in g cm^{-3})	millimetres per year (mm y^{-1})
Grams per square metre per day	$365.25/\rho$ (ρ in kg m^{-3})	millimetres per year (mm y^{-1})

Table 21.28 Corrosion rates of metals

The corrosion rate of a metal in terms of weight loss per unit area ($\text{g m}^{-2} \text{d}^{-1}$) or rate of penetration (mm y^{-1}) can be calculated from Faraday's law if the current density is known. Conversely, the corrosion current density can be evaluated from the weight loss per unit area or from the rate of penetration. The following symbols and units have been adopted in deriving these relationships in which it is assumed that corrosion is uniform and the rate is linear:

m = Mass of metal corroded (g)

M = Molar mass (g mol^{-1})

z = Number of electrons involved in one act of the corrosion reaction

F = Faraday's constant, 96 487 C ($1 \text{ A} \equiv 1 \text{ Cs}^{-1}$)

I = Current (A)

i = Current density (A cm^{-2}) and $i = I/S$

t = Time (s)

ρ = Density of metal (g cm^{-3})

S = Area of metal involved (cm^2)

d = Thickness of metal removed (cm).

From Faraday's law the weight loss per unit area is

$$\frac{m}{S} = \frac{Mit}{zF} \quad (\text{g cm}^{-2}) \quad \dots(21.1)$$

Since $m = \rho Sd$, then from equation 21.1

$$\rho Sd = \frac{Mit}{zF} \text{ or } \rho d = \frac{Mit}{zF} \quad \dots(21.2)$$

and from equation 21.2 the rate of penetration d/t when i is in A cm^{-2} is given by

$$\frac{d}{t} = \frac{Mi}{\rho zF} \quad (\text{cm s}^{-1}) \quad \dots(21.3)$$

If the c.d. i' is in mA cm^{-2} , d in mm and t in years, then

$$\begin{aligned} \frac{d}{t} &= \frac{10^{-1}}{365 \times 24 \times 60 \times 60} = \frac{Mi'}{\rho zF} \times 10^{-3} \quad (\text{mm y}^{-1}) \\ \therefore \frac{d}{t} &= 3.2706 \frac{Mi'}{z\rho} \quad (\text{mm y}^{-1}) \quad \dots(21.4) \end{aligned}$$

To convert rate of penetration into weight loss per unit area per unit time:

$$(\text{g m}^{-2} \text{d}^{-1}) \times \frac{0.36525}{\rho} = (\text{mmy}^{-1})$$

To convert c.d. (mA cm^{-2}) into gmd:

$$(\text{g m}^{-2} \text{d}^{-1}) = 3.2706 \frac{Mi'}{z\rho} \times \frac{\rho}{0.36525} = 8.954 \frac{Mi'}{z} \quad \dots(21.5)$$

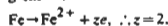
If i'' is the current density in $\mu\text{A cm}^{-2}$

$$(\text{g m}^{-2} \text{d}^{-1}) = 8.954 \frac{Mi''}{z} \times 10^{-3} \quad (21.6)$$

Table 21.29 Corrosion rates of iron at various current densities

Current density	mm y ⁻¹	gm ⁻² d ⁻¹
1 μ A cm ⁻²	0.0116	0.250
10	0.1159	2.501
100	1.1591	25.006
200	2.3181	50.011
300	3.4772	75.017
400	4.6362	100.022
500	5.7953	125.028
600	6.9543	150.034
700	8.1134	175.039
800	9.2724	200.045
900	10.4315	225.050
1 mA cm ⁻²	11.5905	250.056
2	23.1810	500.113
3	34.7715	750.169
4	46.3620	1000.226
5	57.9525	1250.282
6	69.5430	1500.339
7	81.1335	1750.395
8	92.7240	2000.452
9	104.3145	2250.508
10	115.9050	2500.565

Data: molecular weight of Fe = 55.85 g mol⁻¹; density = 7.88 g cm⁻³.

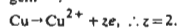


Relationships: (mm y⁻¹) = 11.5905 i' (mm y⁻¹) (i' in mA cm⁻²),
or (mm y⁻¹) = 0.0115905 i'' (mm y⁻¹) (i'' in μ A cm⁻²),
(g m⁻² d⁻¹) = 250.056 i' .

Table 21.30 Corrosion rates of copper at various current densities

Current density	(mm y ⁻¹)	(gm ⁻² d ⁻¹)
1 μ A cm ⁻²	0.0116	0.284
10	0.1161	2.845
100	1.1610	28.449
200	2.3220	56.897
300	3.4830	85.346
400	4.6440	113.795
500	5.8050	142.244
600	6.9659	170.692
700	8.1269	199.141
800	9.2879	227.590
900	10.4489	256.038
1 mA cm ⁻²	11.6099	284.487
2	23.2198	568.974
3	34.8298	853.460
4	46.4397	1137.947
5	58.0496	1422.434
6	69.6595	1706.921
7	81.2695	1991.408
8	92.8794	2275.895
9	104.4893	2560.381
10	116.0992	2844.868

Data: molecular weight of Cu = 63.54 g mol⁻¹; density = 8.95 g cm⁻³.



Relationships: (mm y⁻¹) = 11.6099 i' (i' in mA cm⁻²),
(mm y⁻¹) = 0.0116 i'' (i'' in μ A cm⁻²),
(g m⁻² d⁻¹) = 284.4868 i' .

Table 21.31 Relationship between current density and 1 g m⁻² d⁻¹ or 1 mm y⁻¹ for various metals

Reaction	M (g mol ⁻¹)	A cm ⁻² for 1 g m ⁻² d ⁻¹	ρ (g cm ⁻³)	A cm ⁻² for 1 mm y ⁻¹
Al Al ³⁺ + 3e	26.98	12.42×10^{-6}	2.70	91.811×10^{-6}
Mg Mg ²⁺ + 2e	24.32	9.18×10^{-6}	1.741	43.76×10^{-6}
Fe Fe ²⁺ + 2e	55.85	4.00×10^{-6}	7.88	86.30×10^{-6}
Fe Fe ³⁺ + 3e	55.85	6.00×10^{-6}	7.88	129.45×10^{-6}
Zn Zn ²⁺ + 2e	65.38	3.42×10^{-6}	7.133	66.79×10^{-6}
Cd Cd ²⁺ + 2e	112.41	1.99×10^{-6}	8.65	47.13×10^{-6}
Ni Ni ²⁺ + 2e	58.71	3.80×10^{-6}	8.85	92.07×10^{-6}
Sn Sn ²⁺ + 2e	118.70	1.88×10^{-6}	7.31	37.63×10^{-6}
Pb Pb ²⁺ + 2e	207.21	1.08×10^{-6}	11.36	33.59×10^{-6}
Cu Cu ²⁺ + 2e	63.54	3.51×10^{-6}	8.95	86.01×10^{-6}
Ti Ti ³⁺ + 3e	47.90	6.99×10^{-6}	4.507	86.25×10^{-6}
Ti Ti ⁴⁺ + 4e	47.90	9.33×10^{-6}	4.507	115.13×10^{-6}
Ag Ag ⁺ + e	107.873	1.04×10^{-6}	10.5	29.90×10^{-6}

Calculation:

From equation 21.4 and replacing i' by i (A cm⁻²)

$$i = \frac{3.0575 \rho}{M} \times 10^{-4} \quad (\text{mm y}^{-1})$$

From equation 21.5

$$i = \frac{1.1167 z}{M} \times 10^{-4} \quad (\text{g m}^{-2} \text{ d}^{-1})$$

Table 21.32 Weight and thickness of certain metals deposited by 1 Ah

<i>Metal</i>	<i>Density</i> (g cm ⁻³)	<i>Molecular weight</i> (g mol ⁻¹)	<i>Theoretical weight for 100% efficiency</i> (g)	<i>Theoretical thickness at 100% current efficiency</i> (mm cm ⁻²)	<i>Typical current efficiency (C.E.) obtained in practice</i> (%)	<i>Actual thickness for typical current efficiency</i> (mm cm ⁻²)
Cadmium, Cd ²⁺	8.64	112.40	2.097	2.427	90 (cyanide)	2.184
Chromium, Cr ⁶⁺	7.19	51.996	0.323	0.450	14	0.063
Copper(cyan.), Cu ⁺	8.95	63.54	2.372	2.649	45	1.192
Copper (acid), Cu ²⁺	8.95	63.54	1.186	1.324	97	1.285
Gold, Au ⁺	19.3	196.967	7.356	3.808	77	2.932
Iron, Fe ²⁺	7.88	55.874	1.042	1.322	93	1.230
Lead, Pb ²⁺	11.36	207.19	3.865	3.402	95	3.232
Nickel, Ni ²⁺	8.85	58.71	1.095	1.238	96	1.188
Platinum, Pt ⁴⁺	21.4	195.09	1.821	0.850	35 (approx.)	0.298
Silver, Ag ⁺	10.5	107.870	4.025	3.833	100	3.833
Tin, Sn ²⁺	7.31	118.69	2.214	3.029	93 (acid)	2.817
					78 (stannate)	2.363
Zinc, Zn ²⁺	7.2	65.37	1.219	1.694	98 (acid)	1.660
					87 (cyanide)	1.474

Calculation:

Since 1 Ah = 3600 C, the theoretical weight deposited $m = \frac{3600 M}{96\,500z} \text{ g(Ah)}^{-1}$

The theoretical thickness = $\frac{3600 M}{96\,500zp} \text{ cm (Ah)}^{-1}$ or $\frac{36\,000 M}{96\,500zp} \text{ mm (Ah)}^{-1}$

The actual thickness = $\frac{0.3731M \times \text{C.E.}}{zp} \text{ mm (Ah)}^{-1}$

Table 21.33 Compositions of industrial metals and alloys

Material	Description and composition (%)
Admiralty brass	Cu-29Zn-1Sn
AISI type 4130	Cr-Mo steel: 0.27-0.33% C, 0.75-1.20% Cr, 0.15-0.25% Mo
AISI type 4140	Cr-Mo steel: 0.37-0.44% C, 0.75-1.20% Cr, 0.15-0.25% Mo
Al-Bz9	Cast Al bronze with 8.0-10.5% Al
Alclad 24S-T3	Al-4.5Cu-1.5Mg-0.6Mn, plated with 99.7% Al
Alcoa 3S	Al-1.2Mn; German Werkstoff 3.0515
Alcoa 13 or 13S (Alcan)	Al-12.0Si; German Werkstoff 3.2572
Alcoa 52S	Al-2.5Mg-0.25Cr; German Werkstoff 3.3535
Alcoa 54S	Al-3.5Mg-0.25Cr
Alcoa 61S	Al-1Mg; German Werkstoff 3.2315
Alcoa 356	Al-7Si-0.3Mg; German Werkstoff 3.2341
Aloyco 20	Austenitic steel with 19-21% Cr, 28-30% Ni, 4.0-4.5% Cu, 2.5-3.0% Mo
Aloyco 31	Austenitic steel with 25% Cr, 10% Ni, 3% Mo, 1% Si
Ambrac	Cu-Si alloy with 6.5% Si
Ambrac 850	Cu-20Ni-5Zn
Amoco 8, 12 or 16	Cu-8 to 10Al
Anticorodal I	Al-1.0Mg + Si
Antinit	see Böhler Antinit and Böhler Superantinit
AT-Nickel	min. 99% Ni; welding quality
BA-28	Al-5Mg-0.5Mn (British alloy)
Bergit B	Ni-Mo alloy with 62% Ni, 32% Mo
Bergit C	Ni-Mo alloy with 53% Ni, 19% Mo, 13% Cr, 5% W
Böhler Antinit AS5W	High-alloyed austenitic steel with 17% Cr, 13% Ni + Mo
Böhler Antinit SAS 8	High-alloyed austenitic steel with 18% Cr, 18% Ni, 2% Mo, 2% Cu + Nb; especially for sulphuric acid
Böhler Antinit SAS 10	High-alloyed austenitic steel with 18% Cr, 22% Ni + Mo + Cu + Nb
Böhler Superantinit B (Antinit HB)	64% Ni, 28% Mo + Fe
Böhler Superantinit C (Antinit HC)	60% Ni, 17% Mo, 16% Cr + Fe
BS-Seewasser	Al-3 to 7Mg or Al-3Mg + Si
Cadag	Ag-4Cd
Carpenter 20	Fe-29Ni-20Cr-2Mo-3Cu
Carpenter 20Cb	Fe-29Ni-20Cr-2Mo-3Cu + Nb
Carpenter 20Cb3	High-alloyed steel with 20.1% Cr, 33.9% Ni, 2.3% Mo, 3.3% Cu + Nb
Chlorimet 2	62% Ni, 32% Mo, max. 3% Fe
Chlorimet 3	60% Ni, 18% Mo, 18% Cr, max. 3% Fe
Copper, O.F.H.C. or P.D.C.P.	min. 99.9% Cu (oxygen-free high conductivity*)
Corrix metal	Cu-8 to 10Al-3 to 4Fe
Corronel 220	Ni-Mo alloy with 28% Mo, max. 3% Fe, 2% V
Corronel B (Corronel 210)	Ni-Mo alloy with 66% Ni, 28% Mo, 6% Fe
Croloy 5 Si	Low-C steel with 4-5% Cr, 1-2% Si, 0.45-0.65% Mo
Cron. 2525 Ti	High-alloyed austenitic steel with 24-26% Cr, 24-26% Ni, 2.0-2.5% Mo, max. 2% Si, max. 0.06% C (similar to German Werkstoff 4577)
Cunifer	Cu-10 to 30Ni-2Fe
DIN AlMn	Al-1.25Mn
DIN X5 CrNiMo 1812	Steel with 16.5-18.5% Cr, 12-14% Ni, 2.5-3.0% Mo (similar to German Werkstoff 4436)

*See Vergleich US-Amerikanischer, Britischer und Deutscher Normen auf dem Gebiet der Kupfersorten, Deutsches Kupferinstitut, Berlin (1962).

Table 21.33 (continued)

<i>Material</i>	<i>Description and composition (%)</i>
DIN X5 CrNiMoCuNb1818	High-alloyed austenitic steel with 17-18% Cr, 19-21% Ni, 2.0-2.5% Mo, 1.8-2.2% Cu, max. 0.07% C, Nb > 8 x %C (similar to German Werkstoff 4505)
Dowmetal H	Mg-6Al-3Zn
Duracid	Cast Si-Fe (min. 14.5% Si) with or without Mo
Duralinium	Al-1 to 5Mg-0.3 to 0.6Mn
Duranickel	Ni-4.5Al-0.5Ti
Durichlor	Cast Si-Fe with 14.5% Si and Mo
Durimet 20	Cast steel with 29% Ni, 20% Cr, 2% Mo, 3% Cu, 1% Si
Duriron	Cast Fe, 14.5% Si, 0.8% C
Elcomet K	High-alloyed steel with 22% Ni, 23% Cr, 4% Cu, 2% Mo, 1.3% Si, max. 0.12% C
Elektron	Mg alloy with Zn or Zn + Al and other elements
Elektron AZM	Mg-6Al-1Zn
Euzonit 50	Cast Ni-Mo alloy with 55% Ni, 20% Mo, 20% Fe
Euzonit 50S	Wrought Ni-Mo alloy with 55% Ni, 20% Mo, 20% Fe
Euzonit 60	Cast Ni-Mo alloy with 60% Ni, 20% Mo, 17% Cr
Euzonit 60S	Wrought Ni-Mo alloy with 60% Ni, 20% Mo, 17% Cr
Euzonit 70	Cast Ni-Mo alloy with 67% Ni, 30% Mo
Euzonit 70S	Wrought Ni-Mo alloy with 68% Ni, 30% Mo
Euzonit 85	Cast Ni-Si alloy with 85% Ni, 9% Si
Everbrite	Cu-10 to 30Ni-8Fe
Everbrite 90	Cu-35Ni
Everdur 1000	Cu-4Si-1Mn
Everdur 1010	Cu-3.1Si-1.1Mn
Ferry-Metal	Cu-20Ni or Cu-45Ni
FK-Silver	Ag, little Ni
German silver	Cu-20Ni-5Sn-4.5Pb-6.5Zn
German Werkstoff No. 4000	Steel with 12-14% Cr, 0.08% C
German Werkstoff No. 4122	Stainless steel with 15.5-17.5% Cr, 0.33-0.43% C
German Werkstoff No. 4300	Steel with 18.0% Cr, 9.0% Ni, max. 0.12% C
German Werkstoff No. 4301	Steel with 18.0% Cr, 10.0% Ni, max. 0.07% C
German Werkstoff No. 4401	Steel with 17.5% Cr, 11.0% Ni, 2.2% Mo, max. 0.07% C
German Werkstoff No. 4410	Steel casting with 17-19% Cr, 9-11% Ni, 2.0-2.5% Mo, max. 0.15% C
German Werkstoff No. 4436	Steel with 16.5-18.5% Cr, 12-14% Ni, 2.5-3% Mo, max. 2% Si, max. 0.07% C
German Werkstoff No. 4449	Steel with 17% Cr, 13.5% Ni, 4.5% Mo, max. 0.07% C
German Werkstoff No. 4472	Cast alloy with 60% Ni, 17% Mo, 16.5% Cr, max. 0.10% C
German Werkstoff No. 4505	Steel with 17.5% Cr, 20% Ni, 2.2% Mo, 2% Cu, stabilised with Nb
German Werkstoff No. 4506	Steel with 17.5% Cr, 20% Ni, 2.2% Mo, 2% Cu, stabilised with Ti
German Werkstoff No. 4510	Stainless steel with 17% Cr, stabilised with Ti
German Werkstoff No. 4511	Steel with 16.5-18% Cr, stabilised with Nb
German Werkstoff No. 4523	Stainless steel with 16-18% Cr, 1.5-2.0% Mo, stabilised with Nb
German Werkstoff No. 4541	Steel with 18.0% Cr, 10.5% Ni, max. 0.10% C, stabilised with Ti
German Werkstoff No. 4550	steel with 18.0% Cr, 10.5% Ni, max. 0.10% C, stabilised with Nb
German Werkstoff No. 4571	Steel with 17.5% Cr, 11.5% Ni, 2.2% Mo, max. 0.10% C, stabilised with Ti

Table 21.33 (continued)

<i>Material</i>	<i>Description and composition (%)</i>
German Werkstoff No. 4577	High-alloyed austenitic steel with 24-26% Cr, 24-26% Ni, 2.0-2.5% Mo, max. 0.06% C, stabilised with Ti
German Werkstoff No. 4578	High-alloyed austenitic steel with 24-26% Cr, 24-26% Ni, 2.0-2.5% Mo, max. 0.06% C, stabilised with Nb
German Werkstoff No. 4580	Steel with 17.5% Cr, 11.5% Ni, 2.2% Mo, max. 0.10% C, stabilised with Nb
German Werkstoff No. 4590	Steel with 18% Cr, 20% Ni, 2% Mo, 2% Cu, stabilised with Nb
Gun-metal	Cu-8Sn-4Zn
Guronit GS2	Alloyed cast iron with 25-30% Cr
Hastelloy B	Ni-2.5Co-28Mo-6Fe-1Cr-0.05C
Hastelloy C	Ni-16Mo-15Cr-6Fe-4W-2.5Co-0.08C
Hastelloy D	Ni-10Si-3Cu
Hastelloy F	44-47% Ni, 21-23% Cr, 5.5-7.5% Mo, 1.75-2.5% Ta+Nb, max. 2.5% Co, Fe, other elements; C (wrought) 0.05%, C (cast) 0.12%
H-Monel	see Monel H
Hybnickel D	Ni-Cr steel with 20-30% Cr, 5-10% Ni, 0.25-0.50% C
Hybnickel S	Ni-Cr cast steel with 25% Ni, 20% Cr
Hydronalium	Al alloy with Mg
Illium G	Ni-22Cr-6Fe-6Mo-6Cu
Inalium	Al-2Cd-0.8Mg-0.4Si
Incoloy 825	
(formerly Ni-o-nel)	Ni-31Fe-21Cr-3Mo-1.8Cu-0.05C
Inconel	Ni-15Cr-8Fe
Inconel 600	Ni-14 to 17Cr-6 to 10Fe-max. 0.2C
Inconel X	Ni-15Cr-7Fe-3Ti-1Co
Irrubigo 25	High-alloyed austenitic steel with 18% Cr, 25% Ni, 4% Mo, 0.08% C, some Cu
K-Monel	see Monel K
KS-Seewasser	Al-1.5Mg-1.5Mn-max. 1Sb
Lang alloy 5R	Ni-15 to 18Cr-17Mo-5W-5Fe
LC-Nickel	Low-C nickel, min. 99% Ni, max. 0.02% C
Mangal	Al-1.5Mn
Märker 1818 (SN18)	High-alloyed austenitic cast steel with 18% Cr, 18% Ni, 2% Mo, 2% Cu, 0.08% C
Märker SN25	High-alloyed austenitic cast steel with 18% Cr, 25% Ni, 4% Mo, 2% Cu, 0.1% C
Märker SN42	Cast alloy with 42% Ni, 18% Cr, 5% Mo, 2% Cu, balance Fe
Meehanite CC (formerly KC)	Flake graphite-pearlitic cast iron for general use for solutions with pH less than 2
Meehanite HE	Flake graphite-pearlitic cast iron; all-round material for general use with good thermal shock resistance
Midvale 2024	Fe-26Cr-4Mo
Monel 400	Ni-30Cu-1Mn-max. 0.5Fe
Monel H	Ni-30Cu-2.5 to 3.0Si (cast alloy)
Monel K	Ni-30Cu-3Al-0.5Ti
Monel S	Ni-30Cu-2Fe-4Si
Muntz metal	Cu-40Zn
Nichrotherm NCT 1A	Steel with 20% Cr, 12% Ni, 2% Si
Nichrotherm NCT 3	Steel with 25% Cr, 20% Ni, 2% Si
Nimonic 75	Ni-20Cr-8Fe-0.1C-1Si-0.4Ti (stabilised)
Ni-o-nel	see Incoloy 825
Ni-Resist I	Fe-15Ni-6Cu-2Cr-2.8C

Table 21.33 (continued)

<i>Material</i>	<i>Description and composition (%)</i>
Ni-Resist 2	Alloyed cast iron with 20% Ni, 2.3% Cr, max. 2.0% C
Ni-Resist 3	Alloyed cast iron with 30% Ni, 3% Cr, max. 2.6% C
Packfong	Ni-Cu-Zn-alloy with 40-44% Cu, 31-40% Ni, 15-25% Zn
Pallacid	Au-Ag-Pd alloy with 30% Au, 40% Ag, 30% Pd
Pantal	Al-1.4Mg-0.70Si-0.90Mn-0 to 0.2Ti
Remanit 1880 SSW	Austenitic Cr-Ni steel with 17.5% Cr, 11.5% Ni, 2.3% Mo, max. 0.06% C (similar to U.S. type 316)
Remanit 1880 SW	Austenitic Cr-Ni steel with 18.5% Cr, 11% Ni, max. 0.06% C (similar to U.S. type 304)
Remanit 1990 SS	Stainless steel with 18% Cr, 9.5% Ni, 2% Mo, 2.4% Si
Remanit 2525 SST	High-alloyed austenitic steel with 25% Cr, 25% Ni, 2.2% Mo, Ti-stabilised
Remanit HB	Ni-Mo alloy, Ni-32Mo-1Si-0.15C+Fe
Remanit HC	Ni-Cr-Mo alloy, Ni-15Cr-17Mo-5W-0.15C+Fe
*SAE 1020	Steel with 0.20% C, 0.45% Mn
*SAE 4130	Steel with 0.31% C, 1.0% Cr, 0.20% Mo
*SAE 8630	Steel with 0.30% C, 0.55% Ni, 0.50% Cr, 0.20% Mo
*SEL 4500	Cast high-alloyed austenitic steel with 19-21% Cr, 24-26% Ni, 2.5-3.5% Mo, 1.5-2.5% Cu, Nb-stabilised
*SEL 4505	High-alloyed austenitic steel with 16.5-18.5% Cr, 19-21% Ni, 2.0-2.5% Mo, 1.8-2.2% Cu, Nb-stabilised
*SEL 4541	Austenitic Cr-Ni steel with 17-19% Cr, 9-11% Ni, max. 0.1% C, Ti-stabilised
*SEL 4571	Austenitic Cr-Ni steel with 16.5-18% Cr, 10.5-12.5% Ni, 2.0-2.5% Mo, max. 0.1% C, Ti-stabilised
*SEL 4580	Cast austenitic Cr-Ni steel with 16.5-18.5% Cr, 10.5-12.5% Ni, 2.0-2.5% Mo, max. 0.1% C, Nb-stabilised
*SEL 4585	Cast high-alloyed austenitic steel with 16.5-18.5% Cr, 19-21% Ni, 2.0-2.5% Mo, 1.8-2.4% Cu, 0.08% C, Nb-stabilised
Sicromal 5S	Low-C steel with 4.6% Cr, 1.2% Si, 0.45-0.64% Mo
Sicromal M9	Steel with 0.12% C, 1.0-1.3% Si, 12-14% Cr, 0.8-1.1% Al
Sicromal M10	Steel with 0.12% C, 0.8-1.1% Si, 17-19% Cr, 0.8-1.1% Al
Sicromal M11	Steel with 0.15-0.25% C, 0.8-1.3% Si, 24-26% Cr, 3.5-4.5% Ni
Sicromal M12	Steel with 0.12% C, 1.3-1.6% Si, 23-25% Cr, 1.3-1.6% Al
Sicromal M20/10	Steel with 0.20% C, 1.8-2.3% Si, 19-21% Cr, 11-13% Ni
Sicromal M23/20	Steel with 0.20% C, 1.8-2.3% Si, 24-26% Cr, 19-21% Ni
Silumin	Cast Al with 12-13% Si
S-Monel	see Monel S
Steel	see also under AISI, DIN, German Werkstoff, SAE, SEL and U.S. type
Steel APS 10 M4	Steel with 0.12% C, 2% Cr, 0.35% Al, 0.35% Mo
Stellite 1	Co-33Cr-13W-2.5C
Stellite 6	Co-26Cr-6W-1.0C
Stellite 6B	58% Co, 30% Cr, 4.5% W, 1.0% C, plus some Mo, Ni, Fe
Stellite 12	Co-29Cr-9W-1.8C
Sterling silver	Ag-7.5 to 10Cu
Super Anoxin	Ni-Mo alloy, similar to Hastelloy B
Superantinit	see Böhler Superantinit
Thermisilid E	Cast Si-Fe with 18% Si
Tombac	Cu-Zn alloy with 72-90% Cu

*SAE = Society of Automotive Engineers.
SEL = Stahl und Eisen-Liste.

Table 21.33 (continued)

<i>Material</i>	<i>Description and composition (%)</i>
Toncan enamelling iron	Pure iron with max. 0.03% C
AISI type 201	Austenitic steel with 16–18% Cr, 3.5–5.5% Ni, 5–7.5% Mn, max. 0.15% C
AISI type 202	Austenitic steel with 17–19% Cr, 4–6% Ni, 7.5–10% Mn, max. 0.15% C
AISI type 302	Austenitic steel with 17–19% Cr, 8–10% Ni, 0.08–0.15% C
AISI type 302 B	Austenitic steel with 17–19% Cr, 8–10% Ni, 2–3% Si, max. 0.15% C
AISI type 304	Austenitic steel with 18–20% Cr, 8–11% Ni, 0.08% C
AISI type 304 L	Austenitic steel with 18–20% Cr, 8–11% Ni, max. 0.03% C
AISI type 308	Austenitic steel with 19–21% Cr, 10–12% Ni, 0.08% C
AISI type 309	Austenitic steel with 22–24% Cr, 12–15% Ni, 0.2% C
AISI type 309 Nb	Austenitic steel with 22–24% Cr, 12–15% Ni, 0.2% C, Nb-stabilised
AISI type 310	Austenitic steel with 24–26% Cr, 19–22% Ni, 0.25% C
AISI type 316	Austenitic steel with 16–18% Cr, 10–14% Ni, 2% Mo, 0.1% C
AISI type 316 Nb	Austenitic steel with 16–18% Cr, 10–14% Ni, 2% Mo, 0.1% C, Nb-stabilised
AISI type 317	Austenitic steel with 17–19% Cr, 9–12% Ni, max. 0.1% C
AISI type 330	Austenitic steel with 13–17% Cr, 33–37% Ni, 0.2–0.5% C
AISI type 347	Austenitic steel with 17–19% Cr, 9–12% Ni, max. 0.1% C
AISI type 347 Nb	Austenitic steel with 17–19% Cr, 9–12% Ni, max. 0.1% C, Nb-stabilised
AISI type 430	Ferritic steel with 14–18% Cr, max. 0.12% C
AISI type 430 F	Ferritic steel with 14–18% Cr, max. 0.12% C, some Zr, Mo
AISI type 446 L	Alloyed cast iron with 23–27% Cr, max. 0.35% C, max. 0.25% N
AISI type 410	Martensitic steel with 11–13.5% Cr, max. 0.15% C
AISI type 416	Martensitic steel with 12–14% Cr, max. 0.15% C, Se, Mo or Zr (free machining)
AISI type 420	Martensitic steel with 12–14% Cr, 0.35–0.45% C
AISI type 431	Martensitic steel with 15–17% Cr, 1.25–2.5% Ni, max. 0.2% C
AISI type 44 A	Martensitic steel with 16–18% Cr, 0.60–0.75% C
V2A-E	Austenitic steel with 17–19% Cr, 9–11% Ni, Ti-stabilised
V4A-E	Austenitic steel with 16.5–18.5% Cr, 10.5–12.5% Ni, 2.0–2.5% Mo, Ti-stabilised
V4AX-E	Austenitic steel with 18% Cr, 11.5% Ni, 2–2.5% Mo, Nb-stabilised
V16A-E	High-alloyed austenitic steel with 16.5–18.5% Cr, 19–21% Ni, 2.0–2.5% Mo, 1.8–2.2% Cu, Ti-stabilised
V24A-E	High-alloyed austenitic steel with 24–26% Cr, 24–26% Ni, 2.0–2.5% Mo, Ti-stabilised
Wegucit	Cast iron with 30% Cr
Worthite	Cast steel with 20% Cr, 24% Ni, 3% Mo, 3.3% Si, 1.8% Cu
Zircalloy 3	Zr alloy with 0.2–0.3% Sn, 0.2–0.3% Fe, max. 0.05% C
Zircalloy 4	Zr alloy with 1.5% Sn, 0.2% Fe, 0.1% Cr, 0.005% Ni

Data after Rabald, E., *Corrosion Guide*, 2nd ed., Elsevier (1968).P. WOOD
J. SADOWSKA-MAZUR

21.2 Glossary of Terms*

Activation Overpotential: that part of an overpotential (polarisation) that exists across the electrical double layer at an electrode/solution interface and thus directly influences the rate of the electrode process by altering its activation energy.

Active: freely corroding; the antithesis of passive and immune.

Active Loop: the region of an anodic polarisation curve of a metal comprising the active region and the active-passive transition.

Active-passive Transition: the range of potential between the active (freely corroding) state and the passive state.

Activity (thermodynamic): the thermodynamic activity of an entity, i , is $a_i = \exp(\Delta G/RT)$ where ΔG is the free energy increase of 1 mol of i when it is converted from a standard state (defined as when $a_i = 1$) to any other activity $a_i = x$.

Addition Agent: a substance added to an electroplating solution to produce a desired change in the physical properties of the electrodeposit.

Adhesion: the attractive force that exists between an electrodeposit and the substrate.

Alclad: a composite in which a thin layer of aluminium, or an aluminium alloy of good corrosion resistance, is bonded metallurgically to a high-strength aluminium alloy (of lower corrosion resistance) to provide a combination of these two properties.

Anion: a negatively charged ion; it migrates to the anode of a galvanic or voltaic cell.

Anode: the electrode in a galvanic or voltaic cell at which electrochemical oxidation takes place.

Anode Corrosion Efficiency: the ratio of the actual corrosion rate of the anode to the theoretical rate according to Faraday's Law, expressed as a percentage.

Anode Polarisation: the difference between the potential of an anode passing current and the equilibrium potential of the electrode having the same electrode reaction.

Anodic Protection: reduction of the corrosion rate by making the potential

*Terms used in chemical thermodynamics have not been included and reference should be made to Section 20.3. For paint terms, see Section 14.10.

of the metal sufficiently more electropositive by an external source of e.m.f., so that the metal becomes passive.

Anaerobic: air or uncombined oxygen being absent.

Anaerobic Bacteria (anaerobes): group of bacteria that are unable to multiply in any but a minute trace of oxygen.

Angstrom Unit (Å): $1 \text{ Å} = 10^{-4} \text{ cm} = 10^{-1} \mu\text{m} = 10^{-4} \text{ nm}$ (preferred unit).

Anodising: the formation of oxide films on metals by anodic oxidation of the metal in an electrolyte solution. The term can be used for thin dielectric films but is more particularly applied to thicker films formed on some metals such as aluminium at higher anodic voltages.

Anolyte: the electrolyte solution adjacent to the anode.

Anti-pitting Agent: an addition agent (*q.v.*) which is used to prevent the formation of pits or large pores in an electrodeposit.

Austenite: the γ -modification of iron, having an f.c.c. lattice, which is stable above about 700°C ; the term is also applicable to solid solutions of carbon, chromium, nickel, etc. in γ -iron.

Bainite: a structure produced in carbon and alloy steels by rapid cooling to a temperature above that at which martensite is formed, followed by slower cooling.

Base Potential: *see under Potential.*

Bimetallic Corrosion: corrosion of two metals in electrical contact, in which one metal stimulates attack on the other and may itself corrode more slowly than when it is not in such contact; *galvanic* is often used in place of *bimetallic*.

Code Plot: a graph of the frequency response (*see Frequency Response Analysis*) of an electrode whereby the magnitude and the phase angle are separately plotted as a function of the frequency.

Breakaway Corrosion: a sudden increase in corrosion rate, especially in high-temperature 'dry' oxidation, etc.

Breakdown Potential: *see Critical Pitting Potential.*

Bright Plating: electroplating under conditions whereby the electrodeposit has a high degree of specular reflectivity.

Brightener: an addition agent used specifically to produce an electrodeposit of high specular reflectivity.

Brush Plating: a method of electrodeposition in which the plating solution is applied to the article to be plated by means of an absorbent pad or brush which contains the anode.

Buffer: a substance, or mixture of substances, which when present in an electrolyte solution tends to diminish fluctuations in pH.

Burnt Deposit: a rough, poorly coherent, electrodeposit that results from the application of an excessively high current density.

Calcareous Scale: a scale consisting largely of calcium carbonate and magnesium hydroxide which may be precipitated from a hard water.

Cathode: the electrode of a galvanic or voltaic cell at which electrochemical reduction takes place.

Cathodic Protection*: reduction of the corrosion rate by making the potential of the metal to be protected more negative, so that the current at any anode is reduced while that at any cathode is increased.

*See also list of underground-corrosion and cathodic-protection terms, p. 21:83

Cathodic Reactant: species which is reduced at a cathode.

Catholyte: the electrolyte solution adjacent to the cathode.

Cation: a positively charged ion; it migrates to the cathode in a galvanic or voltaic cell.

Caustic Embrittlement: stress-corrosion cracking of carbon steels caused by the presence of caustic alkali.

Cavitation-corrosion: the wastage of metal caused by the combined action of cavitation and corrosion.

Cavitation Damage: erosion of a solid surface caused by the collapse of vacuum bubbles formed in a fluid.

Cementite: the iron-carbon compound of formula very close to Fe_3C .

Chemical Conversion Coating: a protective or decorative coating which is produced deliberately on a metal surface by a chemical environment.

Chemical Polishing: improvement in the brightness and levelness of a surface finish of a metal by a chemical dissolution reaction.

Composite Plate: an electrodeposit consisting of two or more layers of metals deposited separately.

Concentration Cell: a galvanic cell in which the e.m.f. is due to differences in the concentration of one or more electrochemically reactive constituents of the electrolyte solution.

Concentration (diffusion or transport) Overpotential: change of potential of an electrode caused by concentration changes near the electrode/solution interface produced by an electrode reaction.

Corrosion (of metals): the process of wastage of metals brought about by electrochemical and/or chemical interaction with their environment. The term has been defined in many ways by many authors: for more detail see Section 1.1. (*See also: Bimetallic Corrosion, Breakaway Corrosion, Filiform Corrosion, Fretting Corrosion, Galvanic Corrosion, Graphitic Corrosion, Intergranular Corrosion, Localised Attack, Pitting, Stress-corrosion Cracking, Uniform Corrosion.*)

Corrosion Control: control of the corrosion rate and form of attack of a metal of a given metal/environment system at an acceptable level and at an economic cost.

Corrosion-Erosion *see* Erosion-corrosion.

Corrosion Fatigue: failure by cracking caused by reversing alternating stress in the presence of a corrosive environment.

Corrosion Potential (mixed potential, compromise potential): potential resulting from the mutual polarisation of the interfacial potentials of the partial anodic and cathodic reactions that constitute the overall corrosion reaction.

Corrosion Product: metal reaction product resulting from a corrosion reaction; although the term is normally applied to solid compounds it is equally applicable to gases and ions resulting from a corrosion reaction.

Corrosion Rate: the rate at which a corrosion reaction proceeds. It may be expressed as a rate of penetration mm y^{-1} , $\mu\text{m s}^{-1}$ etc. (inches per year or ipy is still sometimes used), or as a rate of weight loss per unit area, for example: $\text{g m}^{-2} \text{d}^{-1}$, $\text{mg dm}^{-2} \text{d}^{-1}$ (mdd) etc. It may also be expressed as the equivalent current density.

Couple (bimetallic, galvanic): two dissimilar metals in electrical contact.

Covering Power: the ability of a plating solution to produce an electrodeposit

(irrespective of thickness) at low current densities on all significant areas.

Crevice Corrosion: localised corrosion resulting from the presence of a crevice in a fabricated component or between two surfaces, at least one of which is a metal.

Critical Anode Current Density: anodic current density that must be exceeded in order to produce an active to passive transition (for a given metal it varies with the nature of the solution, temperature, velocity, etc.).

Critical Humidity: the relative humidity (r.h.) at and above which the atmospheric corrosion rate of a metal increases markedly.

Critical Pitting Potential: the most negative potential required to initiate pits in the surface of a metal held within the passive region of potentials (it varies with the nature of solution, temperature, time, etc.).

Current (I): the rate of transfer of electric charge; unit current is the ampere (A) which is the transfer of 1 coulomb/second (1 C/s).

Current Density (i): the current per unit area (usually geometric) of surface of an electrode (units: $A\ m^{-2}$, $A\ cm^{-2}$, $mA\ m^{-2}$ etc.).

Current Efficiency: the ratio of the rate of a specified electrochemical reaction expressed as a current or current density (anodic or cathodic) to the total current or current density (anodic or cathodic) flowing. It is usually expressed as a percentage.

Cyclic Voltammetry: measurement of the current or current density as a function of the electrode potential by application of one or more potential sweep cycles.

Deactivation: prior removal of the constituent (of a liquid) that is active in causing corrosion. The term is usually applied to the removal of oxygen by physical and/or chemical methods.

Dealloying: selective removal by corrosion of a constituent of an alloy.

Delayed Failure: *see under Sustained Load Failure.*

Depolarisation: reduction or elimination (by physical or chemical methods) of the electrode polarisation needed to produce a specified current.

Deposit Attack: localised corrosion (a form of crevice corrosion) under and resulting from a deposit on a metal surface.

Dezincification: preferential corrosion of zinc from brass resulting in a copper-rich residue on the surface of the alloy. The term also applies to preferential loss of the zinc component by evaporation at elevated temperature.

Differential Aeration: Differences in oxygen concentration in the electrolyte solution in contact with a metal. Differential aeration stimulates corrosion of that area where the oxygen concentration is lower, which becomes the anodic site.

Diffusion: Movement of atoms, ions or molecules under an activity (or concentration) gradient.

Diffusion Coating: a coating produced by diffusion at elevated temperatures.

Diffusion Layer: the thin layer of solution adjacent to an electrode through which transport of species to or from the electrode surface occurs by diffusion rather than by convection.

Electrochemical Cell: a cell in which chemical energy is transferred into electrical energy.

Electrolytic Cell: a cell in which electrical energy is used to bring about

electrode reactions and is thus converted into chemical energy. (Note: the term 'electrochemical cell' is frequently used to describe both types of cells.)

Electrochemical Equivalent: number of moles of substance reacted electrochemically by the passage of 1 Faraday of charge.

Electrochemical Impedance Spectroscopy: *see* **Frequency Response Analysis.**

Electrode: an electron conductor by means of which electrons are provided for, or removed from, an electrode reaction.

Electrode Potential (E): the difference in electrical potential between an electrode and the electrolyte with which it is in contact. It is best given with reference to the standard hydrogen electrode (S.H.E.), when it is equal in magnitude to the e.m.f. of a cell consisting of the electrode and the S.H.E. (with any liquid-junction potential eliminated). When in such a cell the electrode is the cathode, its electrode potential is positive; when the electrode is the anode, its electrode potential is negative. When the species undergoing the reaction are in their standard states, $E = E^\circ$, the *standard electrode potential*.

Electrodeposition: deposition of a metal or alloy onto a substrate by electrochemical reduction of its ions from an electrolyte under the application of a cathodic overpotential.

Electrogalvanising: galvanising by electroplating.

Electroless Plating: formation of a metallic coating by chemical reduction catalysed by the metal deposited.

Electrolysis: decomposition by the passage of electric current.

Electrolyte: a substance, liquid or solid, which conducts electrical current by movement of ions (not of electrons). In corrosion science, an electrolyte is usually a liquid solution of salts dissolved in a solvent, or a molten salt. The term also applies to polymers and ceramics which are ionically conductive.

Electrolyte Solution: a solution in which the conduction of electric current occurs by the passage of dissolved ions.

Electrolytic Cleaning: cleaning of a metallic surface obtained by making it the anode or cathode of a cell containing a suitable electrolyte solution.

Electron Acceptor: a species in solution that accepts one or more electrons from a cathode for each act of the cathodic reaction and is thus reduced to a lower valence state.

Electromigration of Ions: movement of ions under an electric field.

Electrophoresis: motion of charged colloidal particles immersed in a liquid driven by an electric field.

Electrophoretic Plating (Electrophoretic Deposition): production of a layer or deposit onto an electrode by discharge of colloidal particles from a solution.

Electroplating: deposition of a thin adherent layer of a metal or alloy onto a substrate by electrochemical reduction of its ions from an electrolyte under application of a cathodic overpotential.

Electropolishing: surface finishing of a metal by making it the anode in an appropriate solution, whereby a bright and level surface showing specular reflectivity is obtained.

Ellipsometry: measurement of the characteristics of polarised light after reflection from a surface.

e.m.f Series: a table of the standard equilibrium electrode potentials of systems of the type $M^{z+}(aq.) + ze = M$, relative to the standard hydrogen electrode, and arranged in order of sign and magnitude.

Epitaxy: the phenomenon whereby a deposit or coating takes up the lattice habit and orientation of the substrate.

Equilibrium Potential (E_0): the electrode potential of an unpolarised electrode at equilibrium. At the equilibrium potential there is no net reaction. The potential is controlled by the same electrode reaction occurring anodically and cathodically at an equal rate, called the exchange current density.

Erosion: loss of material mechanically by impact of a liquid, gaseous or particulate environment.

Erosion-corrosion: the wastage of a material caused by the conjoint action of erosion and corrosion by a liquid or gaseous environment, with or without solid particles.

Evans Diagram: diagram in which the E vs. I relationships for the cathodic and anodic reactions of a corrosion reaction are drawn as straight lines intersecting at the corrosion potential, thus indicating the corrosion current associated with the reaction.

Exchange Current Density (i_0): the rate of exchange of electrons (expressed as a current per unit area) between the two components of a single electrochemical reaction when the reaction is in equilibrium. The exchange current density flows only at the equilibrium potential.

Exfoliation: loss of material in the form of layers or leaves from a solid metal or alloy.

Faraday Constant (F): the quantity of electric charge involved in the passage of one Avagadro number (or one mole) of electrons. The value of F (universal) is $96\,485\text{ C mol}^{-1}$.

Faraday's Law: the quantity of charge (Q) passed in an electrochemical reaction is directly proportional to the number of moles (n) of substance reacted. Thus $Q = zFn$, where z is the number of electrons involved in one molecule of the reaction and F is the Faraday constant.

Fatigue: failure of metal under conditions of repeated alternating stress.

Ferrite: the body-centred cubic form of iron (α -iron) and the solid solutions of one or more elements in b.c.c. iron.

Filiform Corrosion: corrosion in the form of hairs or filaments progressing across a metal surface.

Film: a thin coating of material, not necessarily thick enough to be visible.

Flade Potential: the potential at which a metal which is passive becomes active (see **Passivation Potential**).

Fogging: reduction of the lustre of a metal by a film or particulate layer of corrosion product, e.g. the dulling of bright nickel surfaces.

Fouling: deposition of flora and fauna on metals exposed to natural waters, e.g. sea-water.

Frequency Response Analysis: the response of an electrode to an imposed alternating voltage or current signal of small amplitude, measured as a function of the frequency of the perturbation. Also called Electrochemical Impedance Spectroscopy.

Fretting Corrosion: deterioration resulting from repetitive rubbing at the

- interface between two surfaces (fretting) in a corrosive environment.
- Galvanic Cell:** an electrochemical cell having two electronic conductors (commonly dissimilar metals) as electrodes.
- Galvanic Corrosion:** corrosion associated with a galvanic cell (often used to refer specifically to **Bimetallic Corrosion**).
- Galvanostatic Polarisation (intentional static):** polarisation of an electrode during which the current density is maintained at a predetermined constant value.
- Galvanic Series:** a list of metals and alloys based on their relative potentials in a given specified environment, usually sea water.
- Galvanising (hot dip):** coating of iron and steel with zinc using a bath of molten zinc.
- Graphitic Corrosion:** corrosion of grey cast iron in which the metallic constituents are removed as corrosion products, leaving the graphite.
- Green Rot:** carburisation and oxidation of certain nickel alloys at around 1000°C resulting in a green corrosion product.
- Half-cell:** one half of an electrochemical cell, comprising one electrode (anode or cathode) and its immediate electrolyte (anolyte or catholyte).
- Hematite:** an oxide of iron corresponding closely to Fe_2O_3 produced during the oxidation of iron: it is an *n*-type semiconductor in which diffusion of O^{2-} ions occurs via anion vacancies.
- Hydrogen Electrode:** an electrode at which the equilibrium $\text{H}^+ (\text{aq.}) + e \rightarrow \frac{1}{2} \text{H}_2$, is established. By definition, at unit activity of hydrogen ions and unit fugacity of hydrogen gas the potential of the standard hydrogen electrode $E_{\text{H}^+/\frac{1}{2}\text{H}_2}^0 = 0.00 \text{ V}$.
- Hydrogen Embrittlement:** embrittlement caused by the entry of hydrogen into a metal.
- Hydrogen Overpotential (Overvoltage):** the displacement of the equilibrium (or steady-state) electrode potential of a cathode required for the discharge of hydrogen ions at a given rate per unit area of electrode.
- Immunity:** the state of a metal whose corrosion rate is low or negligible because its potential is below (less positive than) that of equilibrium with a very small concentration (or activity) of its dissolved ions. The metal is thus regarded as thermodynamically stable. Pourbaix has suggested that the "small" metal ion concentration be $10^{-6} \text{ mol dm}^{-3}$ (*Atlas of Electrochemical Equilibria in Aqueous Solutions*, p. 71, Pergamon/CEBELCOR, Oxford (1966)).
- Impingement Attack:** localised corrosion resulting from the action of corrosion and/or erosion (separately or conjoint) when liquids impinge on a surface.
- Inhibitor:** a substance added to an environment in small concentrations to reduce the corrosion rate.
- Inseparable Anodes and Cathodes:** anodes and cathodes which cannot be distinguished experimentally although their existence is postulated by theory.
- Interference Films:** thin transparent films which exhibit colours by interference of light in the visible range.
- Intergranular Corrosion:** preferential corrosion at grain boundaries.
- Internal Oxidation (subsurface corrosion):** formation of particles of corrosion product (usually oxide) within the metal matrix beneath the metal surface. The surface may additionally be covered with a film or scale.

Internal oxidation often arises from diffusion of oxygen into the metal matrix at elevated temperature.

Ion: an electrically charged atom or molecule.

Isocorrosion Chart: a chart having temperature and concentration of the corrodent as co-ordinates and curves (isocorrosion curves) of various specified constant corrosion rates of the metal.

Knife-line Attack: severe highly localised attack (resembling a sharp cut into the metal) extending only a few grains away from the fusion line of a weld in a stabilised austenitic stainless steel, which occurs when the metal comes into contact with hot nitric acid and is due to the precipitation of chromium carbides.

Leveller: a substance which is added to a plating bath to produce a levelling or smoothing action.

Levelling Action: the ability of a plating bath to produce a surface which is smoother than that of the substrate.

Limiting Current Density: the current density at which change of polarisation produces little or no change of current density.

Linear Oxidation: oxidation of a metal in such a way that the rate of oxidation is independent of time.

Linear Polarisation: the linear relationship between potential and current density that is considered to prevail at potentials very close to the corrosion potential.

Liquid Metal Embrittlement: the embrittlement of a metal or alloy as a consequence of contact with a liquid metal, resulting in the formation of cracks.

Local Anodes and Cathodes: the separate anodic and cathodic sites on a single material immersed in a reactive environment.

Localised Corrosion (or localised attack): accelerated corrosion at certain sites only of a metal surface, usually induced by spatial separation of the anodic and cathodic sites. Examples include pitting corrosion, stress-corrosion cracking and intergranular corrosion.

Matt Surface: a surface of low specular reflectivity.

Metal Distribution Ratio: the ratio of the thicknesses of metal produced during electroplating on two specified parts of the cathode.

Metal Spraying: application of a metal coating to a surface (metallic or non-metallic) by means of a spray of metal particles. The metal particles may be produced by 'atomising' a metal wire in a flame-gun or by introducing metal powder into a similar gun.

Migration of Ions: movement of ions towards the anode or cathode under an electric field.

Mil: 0.001 inch or one thousandth of an inch (1 mil = 25.4 μm).

Millscale: thick oxide layer on metals produced during fabrication by hot-rolling; most of the oxidation occurs as the metal passes from one rolling-mill to the next.

Negative Potential: *see under Potential.*

Nernst Equation: the thermodynamic relationship between the equilibrium potential of an electrochemical reaction and the activities of the species involved in that reaction.

Noble Potential: *see under Potential.*

Normal Electrode Potential: *see under Electrode Potential.*

- Nyquist Plot:** a graph of the frequency response of an electrode in which the imaginary component of the impedance is plotted as a function of the real component for a range of frequencies.
- Occluded Cell:** a corrosion cell of a geometry that prevents intermingling of the anodic reaction products (anolyte) with the bulk solution, resulting in a decrease in pH of the anolyte; shielded areas or pits, crevices or cracks in the surface of the metal are examples.
- Open-circuit Potential:** the potential of an electrode (relative to a reference electrode) from which no net current flows, so that the anodic and cathodic reactions occur at an equal rate.
- Overpotential (overvoltage, polarisation):** the displacement from the equilibrium (or steady-state) electrode potential required to cause a reaction to proceed at a given rate.
- Oxidation:** loss of electrons by a species during a chemical or electrochemical reaction; addition of oxygen or removal of hydrogen from a substance.
- Oxidising Agent:** a substance that causes oxidation of another species.
- Oxygen Concentration Cell:** *see under Differential Aeration.*
- Parabolic Oxidation:** oxidation of a metal to produce an oxide film in such a way that the rate of oxidation is proportional to the reciprocal film thickness. Thus if x is the film thickness at time t , then $dx/dt \propto x^{-1}$.
- Partial Reactions:** anodic reaction (reactions) and cathodic reaction (reactions) constituting a single exchange process or a corrosion reaction.
- Partial Current (current densities):** the currents (current densities) corresponding with each of the partial reactions.
- Parting:** selective dissolution of one metal (usually the most electro-reactive) from an alloy leaving a residue of the less reactive constituents.
- Passivation Potential:** the potential at which a metal in the active state becomes passive.
- Passivator:** a substance which in solution causes passivity.
- Passivity:** the state of a metal in which a low corrosion rate is brought about by reaction with its environment under a high anodic driving force through formation of a surface barrier film, usually an oxide.
- Patina:** a green coating of corrosion products of copper (basic sulphate, carbonate and chloride) which forms on copper or copper alloys after prolonged atmospheric exposure.
- pH:** a measure of the hydrogen ion activity defined by $\text{pH} = -\log a_{\text{H}^+}$ where a_{H^+} is the activity of the hydrogen ion.
- Pickle, Pickling:** a solution (usually acidic) used to remove or loosen corrosion products from the surface of a metal.
Anodic and cathodic pickling are forms of electrolytic pickling in which the metal is anodically or cathodically polarised in the pickle.
- Pilling-Bedworth Ratio:** the ratio of the volume of an oxide film on a metal to the volume of metal used to form that oxide.
- Pits (in electroplating):** macroscopic channels in an electrodeposit which may or may not extend to the substrate.
- Pitting (pitting corrosion):** the formation of small holes in an otherwise passive metal surface as a consequence of locally accelerated corrosion.
- Pitting Potential:** minimum potential (least noble or least positive) at which a metal undergoes permanent pitting corrosion.
- Polarisation (overpotential, overvoltage):** difference of the potential of an

electrode from its equilibrium or steady-state potential.

Polarisation Curve: A plot of the current density flowing from an electrode against the electrode potential, often presented on a logarithmic current density axis.

Polarisation Resistance: slope of the linear plot of overpotential versus current density measured at potentials close to the corrosion potential, or the tangent of such a curve at the corrosion potential if the plot is not linear. If a small change in potential, ΔE , gives rise to a change in current density, Δi , then the polarisation resistance is $R_p(\Omega \text{ m}^2) = \Delta E / \Delta i$.

Potential-pH Equilibrium Diagram (Pourbaix Diagram): diagram of the equilibrium potentials of electrochemical reactions as a function of the pH of the solution. The diagram shows the phases that are thermodynamically stable when a metal reacts with water or an aqueous solution of specified ions.

Pores, Porosity (in coatings): microscopic channels in coatings (metallic or non-metallic) which extend to the substrate.

Positive Potential: *see under Potential.*

Potential: potential difference at an electrode defined with reference to another specified electrode.

base potential: a potential towards the negative end of a scale of electrode potentials. The potential of an electrode which is made cathodic is said to become 'more base' or 'more negative' (preferred term).

negative potential: a potential more negative than the potential of the standard hydrogen electrode, e.g. $E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.76 \text{ V}$.

noble potential: a potential towards the positive end of a scale of electrode potentials. The potential of an electrode which is made anodic is said to become 'more noble' or 'more positive' (preferred term).

positive potential: a potential more positive than the potential of the standard hydrogen electrode, e.g. $E_{\text{Cu}^{2+}/\text{Zn}}^{\circ} = +0.34 \text{ V}$.

(*See also Corrosion Potential, Electrode Potential, Equilibrium Potential, Flade Potential, Open-circuit Potential, Passivation Potential, Protection Potential, Redox Potential.*)

Potentiostatic Polarisation: polarisation of an electrode during which the potential is maintained at a predetermined constant value by means of a *potentiostat*.

Pourbaix Diagram: *see Potential-pH Equilibrium Diagram.*

Protection Potential for Pitting: potential below which new pits cannot be initiated nor pre-existing pits continue to propagate.

Rack: a frame for suspending and carrying current to articles during plating and related operations.

Rate-determining Step (r.d.s.): the slowest step in the mechanism of a reaction which thereby controls the rate of the overall reaction. The r.d.s. has the highest activation energy.

Rebar: an abbreviation of reinforcing bar, referring to reinforced concrete.

Redox: abbreviation for reduction-oxidation.

Redox Potential: the equilibrium electrode potential of a reversible reduction-oxidation reaction, e.g. Cu^{2+}/Cu , $\text{Fe}^{3+}/\text{Fe}^{2+}$, Cl_2/Cl^- .

Redox Reaction: a reversible reduction-oxidation reaction.

Reducing Agent: a substance that causes reduction of another species.

Reduction: a chemical or electrochemical reaction in which a species gains

electrons; the removal of oxygen or the addition of hydrogen.

Reference Electrode: an equilibrium (reversible) electrochemical half-cell of reproducible potential against which an unknown electrode potential can be measured. Examples of those commonly used in corrosion are the Pt, H_2/H^+ (the hydrogen electrode), $Hg/Hg_2Cl_2/Cl^-$ (the calomel electrode), $Cu/CuSO_4/Cu^{2+}$, $Ag/AgCl/Cl^-$, all with fixed activities of the dissolved ions.

Relative Humidity: the ratio of the amount of water vapour present in the atmosphere at a given temperature to the amount required for saturation at the same temperature, expressed as a percentage.

Reversible Electrode: an electrode of high exchange current density.

Reversible Potential: *see under Equilibrium Potential.*

Rusting (rust): corrosion of iron or ferrous alloys resulting in a corrosion product which consists largely of hydrous ferric oxide.

Saturation Index: an index which shows if a water of given composition and pH is at equilibrium, supersaturated or unsaturated with respect to calcium carbonate (or to magnesium hydroxide).

Scale: a thick visible oxide film formed during the high-temperature oxidation of a metal (the distinction between a film and a scale cannot be defined precisely).

Season Cracking: cracking resulting from the combined effect of corrosion and stress, which is usually confined to the stress-corrosion cracking of brass in ammoniacal environments.

Selective Leaching: *see Parting.*

Sensitisation: susceptibility to intergranular attack in a corrosive environment resulting from heating a stainless steel at a temperature and time that results in precipitation of chromium carbides at grain boundaries.

Sherardising: the coating of iron and steel with zinc by heating in contact with zinc powder at a temperature below the melting point of zinc.

Shield: a non-conducting medium which is used for altering the current distribution on a cathode or anode.

Spalling: the break-up of a surface through the operation of internal stresses, often caused by differential heating or cooling.

Standard Electrode Potential (E^θ): the equilibrium potential of an electrode reaction when the components are all in their standard states.

Steady-state Potential: the potential of an electrode which is independent of time because its reaction occurs at a constant rate.

Stoichiometric Number: number of times the rate-determining step must occur for one act of the overall reaction.

Stray-current Corrosion: corrosion caused by stray currents flowing from another source of e.m.f. (usually d.c.).

Stress Intensity Factor $K_{I, s.c.c.}$: a fracture toughness parameter used for evaluating susceptibility to stress-corrosion cracking (the subscript I signifies a tensile mode of stressing).

Stress-corrosion Cracking: cracking produced by the combined action of corrosion and static tensile stress (internal or applied).

Strike (n.): an electrolyte solution used to deposit a thin initial film of a metal.

Strike (vb): to electroplate for a short time at a higher initial current density than is normally used.

Stripping: removal of a metal coating by means of an electrolyte solution (or an electrolyte solution and external e.m.f.).

Subscale Formation: *see under Internal Oxidation.*

Substrate: the basis metal on which a coating is present.

Subsurface Corrosion: *see under Internal Oxidation.*

Sulphate-reducing Bacteria (S.R.B.): a species of anaerobic bacteria (*devibrio desulphuricans*) that is capable of causing rapid corrosion of iron and steel in near-neutral solutions in the absence of dissolved oxygen.

Sustained Load Failure: delayed failure due to the presence of hydrogen in stressed high-tensile steels.

Symmetry Factor: ratio of distance across the double layer to summit of energy barrier/distance across the whole double layer.

Tafel Equation: the linear relationship between the overpotential (or potential) and the logarithm of the current density for an electrode reaction in which charge transfer is rate-determining. If η is the overpotential, and i the current density, then $\eta = a + b \log i$, or $\eta = b \log (i/i_0)$ where i_0 is the exchange current density. b is called the Tafel slope expressed in V when the current is expressed on a natural logarithm scale, or V per decade when the current is expressed in decadic logarithms.

Tarnish: dulling, staining or discoloration of metals due to the formation of thin films of corrosion products. (The term can also be applied to thin transparent film which may give rise to interference colours.)

Thief: an auxiliary cathode which is placed in a position relative to the article to be electroplated so that the current density on certain areas is reduced.

Throwing Power: a measure of the ability of an electroplating solution to give a uniform plate on an irregularly shaped cathode.

Transfer Coefficient α : the transfer coefficient of a cathodic process is the fraction of the electrical energy difference $zF\Delta\phi$ that assists the transfer of an ion through the double layer towards the electrode and inhibits its transfer in the reverse direction or vice versa for an anodic process; frequently experimental values of α are approximately 0.5.

Transpassivity: active behaviour of a metal at potentials more positive than those leading to passivity.

Transport of Ions: the combined motion of ions in an electrolyte (solid or liquid) under diffusion and migration.

Transport Number: the proportion of the current carried by a particular ion (transfer number).

Tuberculation: localised attack in which the corrosion products form wart-like mounds over the corroded areas.

Uniform Corrosion (general corrosion): corrosion in which no distinguishable area of the metal surface is solely anodic or cathodic, i.e. anodes and cathodes are *inseparable*, cf. localised corrosion.

Voltaic Cell: a term sometimes used for an electrochemical cell; it is sometimes used to refer to a cell in which chemical changes are caused by the application of an external e.m.f.

Weld Decay: localised attack of austenitic stainless steels at zones near a weld, which results from precipitation of chromium carbides.

Terms used in Cathodic Protection and Underground Corrosion*

Anode Lead: the electrical connection between the anode and the power unit in impressed-current schemes; normally a copper-cored plastics-sheathed standard electric cable.

Anode Shield: protective covering of insulating material placed on a painted structure in the immediate vicinity of the anode to reduce the cathodic current density in that area, thus preventing the development of excessive alkalinity and stripping of the paint (*see Saponification*).

Attenuation*: the decrease in potential and current density along a long buried or immersed structure from the drainage point.

Attenuation Curves: a graph of interfacial electrical potentials between the pipe and surrounding soil in cathodic protection schemes vs. the length of the pipe.

Backfill: the soil replaced over the pipe in the trench (general connotation). In cathodic protection, special backfills are packed around the anodes. These backfills are selected to lower circuit resistance of the anode; for sacrificial anodes a gypsum/bentonite mixture is used, and for impressed-current anodes, coke breeze.

Bond*: a conductor, usually of copper, that connects two points on the same structure or on different adjacent structures, and thus prevents significant differences in potential between two points.

Cantilever Anode: anode supported as a cantilever.

Cathode Lead: the electrical connection from the negative terminal of a d.c. power unit.

Cathodic Protection Rectifier: transformer-rectifier arrangement for supplying the direct current which flows between a groundbed and a buried structure which is receiving cathodic protection.

Continuity Bond: electrical connection made to connect together adjacent sections of a buried structure in order to ensure its electrical continuity.

Corrosion Interaction (or interaction): increase (or decrease) in the rate of corrosion of a buried or immersed structure caused by interception of part of the cathodic protection current applied to another buried or immersed structure.

Current Drainage Survey: a survey to determine current requirements for cathodic-protection schemes. A temporary groundbed is installed at a suitable location and an impressed current is applied between it and the pipe or other structure. A survey of potentials along the structure will produce attenuation curves, and permits fairly accurate estimation of initial current requirements.

Direct Electric Drainage: a means of electric drainage comprising the employment of permanent metallic connections.

Drainage Bond*: bond to effect drainage (*see Drainage*, definition (b)).

*These terms are derived from various sources, principally from the *List of Definitions of Essential Telecommunications Terms (Part I, Corrosion)*, International Telecommunications Union, Geneva, 1957, 1st Supplement, 1960, and the B.S.I. Code of Practice for Cathodic Protection, CP1021: 1973; terms taken from the Code of Practice are marked with an asterisk.

Drainage (electric drainage)*: (a) flow of positive current through the soil or the electrolyte solution from the cathodically protected structure to the groundbed of the impressed current system, or (b) protection of an immersed structure from electrochemical corrosion by making an electrical connection between the structure and the negative return circuit (rail, feeder, busbar) of a d.c. electric traction system.

Drainage Point: the location in a cathodic-protection installation where the cathode lead is attached to the pipe; normally the point of maximum negative potential of the pipe, though this is not always the case when an area of low-resistance soil is adjacent to the drainage point.

Earth*: (a) the conducting mass of earth or of any other conductor in direct electrical connection with earth, (b) a connection, intentional or unintentional, between a conductor and earth.

Electric Drainage: means of electric protection of an underground system against the corrosive action of stray currents arising from a d.c. electric traction system employing one or more connections (drainage bonds) made between the system to be protected and the return circuit of the traction system (rail, return current feeder, negative busbar of the sub-stations).

Electro-osmosis: passage of a liquid through a porous medium (such as a soil) under the influence of a potential difference.

Flood Coat: application of coal-tar or bituminous coatings to pipelines by flooding the heated coating materials over the pipe surface; wrappings and slings are used to pull the coat underneath the pipe.

Forced Drainage*: form of drainage in which the connection between the protected structure and a traction system includes a source of direct current.

Groundbed: in cathodic protection of underground structures, a buried mass of inert material (e.g. carbon), or scrap metal connected to the positive terminal of a source of e.m.f. to a structure.

Holiday: a flaw, often in the form of a pinhole, in a protective organic coating.

Holiday Detector: a high-voltage low-current output generator with a built-in spark gap used for detecting pinholes (holidays) in pipeline coatings.

Impressed Current: cathodic current supplied by a d.c. source to a structure in order to lower the potential to the protective potential for cathodic protection.

Insulating Flange*: flanged joint between adjacent lengths of pipe in which the nuts and bolts are electrically insulated from one or both of the flanges and the jointing gasket is non-conducting, so that there is an electrical discontinuity in the pipeline at that point.

Interaction: *see* Corrosion Interaction.

Interaction Testing: routine investigation carried out when installing cathodic protection schemes on pipelines. The accepted criterion in the UK is that when the secondary structure potential has been moved more than 0.02 V in a positive direction, steps must be taken to eliminate the interaction.

Line Wrapping: the technique of wrapping a pipeline over the pipeline trench; applied only to welded steel pipelines. It is carried out by a line-wrapping machine which travels along the pipe, cleaning it, priming it,

- pulling in the reinforcement, and, if necessary, applying the outer wrap.
- Locating and Bonding:** when cathodic protection is applied to an existing jointed pipeline, all joints must be located without digging up the pipe. On location, each joint is exposed and an electrically conducting bond (usually galvanised steel strip or copper cable) is welded into position.
- Polarised Electric Drainage:** a means of electric drainage comprising the employment of metallic connections between the underground cable system and the traction return circuit, with the insertion of a unidirectional system (rectifier or contactor and relays) in the connections.
- Primary Structure*:** a buried or immersed structure cathodically protected by a system that may constitute a source of corrosion interaction with another (secondary) structure.
- Protection Current:** current made to flow into a metallic structure in order to effect cathodic protection.
- Protective Potential:** an optimum negative potential at which pipe protection is accepted as being sufficient in cathodic-protection schemes. It is a negative potential of the pipe/environment interface, and is applicable to steel when the potential is more negative than -0.85 V vs. a Cu/CuSO₄ electrode located as close to the pipe as practicable. When sulphate-reducing bacteria are present in soil the value should be -0.95 V. An alternative criterion for steel is to change the pipe potential 0.3 V in a negative direction. Similar criteria are applicable to steel in natural waters.
- Reactive (active, sacrificial) Anode:** a mass of metal (Mg, Zn, Al) which, buried or immersed and connected to a metallic structure which is to be protected, forms a cell with that structure and has the effect of making it more negative with respect to the surrounding environment.
- Remedial Bond*:** a bond established between a primary and secondary structure in order to eliminate or reduce corrosion interaction.
- Remote Potentials:** in dealing with a pipeline cathodic-protection system, it is often advantageous to refer all measurements to a half-cell located at a distance from the pipe. Such measurements are referred to as *remote potentials*.
- Resistance Bond*:** a bond either incorporating resistors or of adequate resistance in itself to limit the flow of current.
- Sacrificial Anode:** *see under Reactive Anode.*
- Safety Bond*:** a bond connecting the metallic carcass of a piece of electrical apparatus with earth, in order to limit the rise in potential of the carcass above earth caused by the passage of any fault current or excessive leakage current, and so reduce the risk of electric shock to anyone touching the carcass.
- Saponification:** deterioration by softening of paint film caused by action of aqueous alkali, resulting from cathodic protection at excessively high current densities, on the fatty-acid constituents of the film.
- Sensing Electrode*:** a permanently installed reference electrode used to measure the structure/electrolyte solution potential and to control the protection current.
- Stray Currents:** currents flowing in the soil and arising from electric installations parts of which are not insulated from the soil.
- Structure/Soil Potential:** potential measured between a buried structure and

a suitable non-polarisable electrode, placed in the soil or water as near to the structure as possible; when the value is being indicated the type of electrode used should be clearly stated.

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21.3 Symbols and Abbreviations

Basic SI Units

<i>Quantity</i>	<i>Name</i>	<i>Symbol</i>
length	metre	m
mass	kilogram	kg
time	second	s
force	newton	N
work	joule	J
power	watt	W
current	ampere	A
charge	coulomb	C
e.m.f. and p.d.	volt	V
resistance	ohm	Ω
conductance	siemens	S
inductance	henry	H
capacitance	farad	F
amount of substance	mole	mol

\AA	Angstrom unit
a_A	relative activity (dimensionless) of component A
ABS	acrylonitrile butadiene styrene
a.c.	alternating current
Ah	ampere hour
aq.	aqueous, hydrated
α	transfer coefficient
b.p.	boiling point
β	symmetry factor
$C_{p,m}$	molar heat capacity at constant pressure ($\text{JK}^{-1} \text{mol}^{-1}$)

*The abbreviations N (normal) and M (molar), although not S.I. units, have been retained in the book when these units have been used by authors of published work.

<i>c</i>	concentration (mol m^{-3} , mol dm^{-3})*
CAB	cellulose acetate butyrate
c.d.	current density
CHC	cyclohexylamine carbonate
cm	centimetre
$^{\circ}\text{C}$	degree Celsius (Centigrade)
<i>D</i>	diffusion coefficient ($\text{m}^2 \text{s}^{-1}$, $\text{cm}^2 \text{s}^{-1}$)
<i>d</i>	differential
∂	partial differential; thickness of diffusion layer (m, cm)
Δ	difference, finite change
d	day
dia.	diameter
d.c.	direct current
DCHN	dicyclohexylamine nitrate
dia.	diameter
dm	decimetre
DPN	diamond pyramid number
e.m.f.	electromotive force
<i>E</i>	e.m.f., potential (V)
E°	standard e.m.f., standard electrode potential
$E_{\text{eq.}}$, E_r	equilibrium or reversible e.m.f. or potential
E_{cell}	e.m.f. of cell
E_a	anode potential
E_c	cathode potential
$E_{\text{corr.}}$	corrosion potential
E_{pp}	passivation potential
E_b	breakdown or pitting potential (E_c is also used)
E_p	protection potential
E^{\ddagger}	activation energy (J mol^{-1})
<i>e</i>	elementary charge (proton or electron) (C)
eV	electron volt
exp	exponential function
η_a	anode overpotential (V)
η_c	cathode overpotential
η_A	activation overpotential
η_T	transport, concentration or diffusion overpotential
η_R	resistance overpotential
F	Faraday constant (C mol^{-1})
f, p^*	fugacity (N M^{-2} or Pa)

G	Gibbs free energy (free enthalpy) (J)
G°	standard Gibbs free energy (J)
Γ	Gibbs surface excess (free energy)
g	gram
g.m.d.	grams per square metre per day ($\text{gm}^{-2} \text{d}^{-1}$)
H	enthalpy
HB	Brinell hardness number
HV	Vickers hardness number
h	hour
I	current (A)
i, j	current density (Am^{-2} , Acm^{-2})
$i_{\text{corr.}}$	corrosion c.d.
i_a	actual anodic c.d. measured
i_c	actual cathodic c.d. measured
i_0	equilibrium exchange current density
i_l	cathodic current density for exchange I
i_l	anodic current density for exchange I
i_L	limiting (or maximum c.d.)
i.d.	internal diameter
i.p.y.	inches per year (in y^{-1})
I	ionic strength (mol kg^{-1})
J	electrochemical equivalent
$K_{\text{p/p}}$	equilibrium constant for gaseous system (dimensionless)
$K_{\text{m}\gamma/\text{m}}$	equilibrium constant for solution (dimensionless)
k	rate constant (mol s^{-1})
\overrightarrow{k}	rate constant of a cathodic reaction
\overleftarrow{k}	rate constant of an anodic reaction
κ	electric conductivity (S m^{-1})
K	degree Kelvin
l	length (m, cm)
l, ℓ	litre
ln, ℓn	natural logarithm
log	logarithm to the base 10
m	molecular mass (kg)
M	molar mass (kg mol^{-1})
m.d.d.	$\text{mg dm}^{-2} \text{d}^{-1}$
m.p.y.	mm y^{-1}
ml	millilitre
min	minute

m.p.	melting point
mol	moles
N_0, N_A	Avogadro constant
n	number of moles
n_+	transference number of cation
n_-	transference number of anion
ν	kinematic viscosity
o.d.	outside diameter
ω	angular speed of rotation
Pa	pascal (N m^{-2})
P(J)	permeation rate
p	pressure
pH	$-\log a_{\text{H}^+}$
p.p.m.	parts per million
$\psi(\phi)$	potential of a charged interface
p.t.f.e.	polytetrafluoroethylene
p.v.c.	polyvinylchloride
R	electric resistance; gas constant
ρ	density; oxide/metal volume ratio
r.d.s.	rate-determining step of reaction
$S(A)$	area
S	entropy
s	second
S.C.E.	saturated calomel electrode
S.H.E.; N.H.E.	standard (normal) hydrogen electrode
s.g.	specific gravity
σ	surface charge; stress
T	absolute temperature
θ	surface coverage
t	time
t_f	time to fracture
μ	chemical potential (J)
μ°	standard chemical potential (J mol^{-1})
U	internal energy
U.T.S.	ultimate tensile strength
v	velocity
V	volume
\bar{V}	partial molar volume
VCI	volatile corrosion inhibitor
VPI	Vapour Phase Inhibitor (trade name)
VPN	Vickers pyramid number

v/v	volume for volume
$v/wt.$	volume for weight
$wt\%$	weight percent
$wt./v$	weight for volume
x_A	mole fraction of component A
$z(n)$	number of electrons involved in one act of the reaction (or in the r.d.s.); charge on ion

21.4 Calculations Illustrating the Economics of Corrosion Protection

Each protective system has its own pattern of capital and running costs. Choosing the optimum alternative requires care because some of the factors can be measured precisely while others cannot, and the costs arise at different points in time.

A quick comparison of systems is to compare present first cost + maintenance costs (including access and disruption) in each case. This can be elaborated as follows:

- Step 1* Set out the alternatives, ensuring that there is the same basis of comparison. Eliminate capital and revenue costs common to all protection systems. Write in the extra capital arising from the need to protect the structure. This capital cost may be a direct quotation from a processor or be calculated (*see* Note 3 below). Make sure quotations or calculations refer to the same data.
- Step 2* Add extra transport costs (e.g. when work goes to specialist processing plant instead of direct to site) and extra mark-up (the contractor will add a percentage on subcontracted work) where appropriate and where not included in Step 1.
- Step 3* Deduct tax allowances. Typically for limited liability companies in the UK these comprise initial grants for certain projects in development areas plus first year allowances, adjusted for corporation tax.
- Step 4* Estimate the time required for each system to be complete on site. For the longer time systems enter the cost in interest of this delay assuming the capital sums involved could have been otherwise employed during the extra time required (compared with the quickest system).
- Step 5* Estimate maintenance costs (after making allowance for tax relief) over life of structure including access costs such as scaffolding. In general the future maintenance costs must be estimated making allowance for inflation and then discounted to present values (*see* maintenance terms in equation below).

Step 6 Estimate disruption during maintenance (or erection). As with maintenance costs these can be entered at present costs of such disruption whenever interest rates equal inflation rate.

Table 21 A1 Model cost calculation

	<i>Competing systems</i> (conforming to systems under same environment and same time to first maintenance)	
	<i>first system</i>	<i>second system etc.</i>
Extra capital cost (Step 1)		
Add extra transport costs (Step 2)		
Add extra fabricator's mark-up (Step 2)		
Total gross extra capital cost		
Deduct total taxed allowances (Step 3)		
Total gross extra capital cost net of tax allowances etc.		
Delay factor (Step 4)		
Maintenance costs (Step 5)		
Disruption factor (Step 6)		
Total cost of system, over and above costs common to all systems, and expressed in present value terms		

The maintenance costs and the initial cost are frequently assessed as the Net Present Value (N) which represents the sum of money that must be set aside to now cover both initial and maintenance costs over the total life required.

$$N = F + \frac{M_1}{(1+r)^{P_1}} + \frac{M_2}{(1+r)^{P_2}}$$

where F = first cost of the protective system

M_1 = the cost of maintenance in the year P_1

M_2 = the cost of maintenance in the year P_2 etc.

r = the interest (or 'discount') rate (NB: 12% rate is written 0.12, etc.)

P_1 = the number of years to first maintenance

P_2 = the number of years to second maintenance, etc.

Maintenance costs are steadily rising and we must adjust maintenance costs at present-day values (M) to allow for inflation at an annual rate of r_1 (Note: r_1 is expressed like r).

i.e.

$$N = F + \frac{M(1+r_1)^{P_1}}{(1+r)^{P_1}} + \frac{M(1+r_1)^{P_2}}{(1+r)^{P_2}}$$

In the simplest case where the rate of inflation of maintenance costs is the

same as the interest (or 'discount') rate available on money i.e. where there is no time value of money $r_1 = r$ and the formula simplifies to

$N = F +$ the sum of all maintenance costs at present-day rates
 = the aggregate of all initial and maintenance costs at present-day rates

Similarly other costs can be treated as for the maintenance costs or for the first cost, as appropriate.

Note 1 Present day economics usually favour a protective scheme adequate for the full design life of the structure.

Note 2 For many protective schemes initial cost in the factory is roughly proportional to total thickness but life to first maintenance is not necessarily proportional to thickness e.g. relatively thin metal coatings in certain environments often have the longest lives to first maintenance.

Note 3 Calculation of protection costs from fundamentals has been dealt with in industry orientated handbooks e.g. *Galvanising for Profit*, Galvanisers Association, London, UK. In principle first costs include:

Materials

Labour

Overheads (including inspection; access equipment and tools for painting)

These are usually of the same order of magnitude, with materials being most costly for metal coatings and labour most costly for paint coatings.

Note 4 Surface preparation for painting is often analysed separately as it may typically form one-third of the total cost. Poor surface preparation can more than halve the life expectancy of a coating (and add over 100% to the total life cost) but save less than 20% of the total capital cost. Correct choice of blasting equipment (e.g. nozzle size, grade of abrasive) can save up to half the surface preparation cost.

Note 5 In calculating paint requirements up to 50% more than the theoretical dry film weight requirement should be allowed to cover thick coatings, wastage, repairs, losses (typically 30% for air spray; 15% airless spray; 10% electrostatic spray; 5% roller or brush) etc. Manufacturers should be asked to quote percentage volume solids in their paint to facilitate calculations.

Note 6 Labour costs for the application of paint increase in the order

	airless spray	normal air spray	roller	brush
ratio	1	2	3	4

Brush application is very desirable for inhibitive primers applied directly to steel and for toxic materials. Roller application is not recommended for structural steel surfaces.

- Note 7* Comparative costs (unlike actual costs) change little with time. When labour costs are rising more rapidly than material costs, painting will become slightly more expensive relative to metal coatings and vice versa.
- Note 8* Metal spray, paint powder and tape coatings are usually costed by the area covered which should be known reasonably accurately. Galvanising is costed by weight of steel coated i.e. by thickness of steel. Costs also vary by product.
- Note 9* The most economical system for one job is not necessarily the most economical for another, e.g. galvanised steel may be best for a bolted job but not so where much site welding is necessary.
- Note 10* First costs include access costs e.g. scaffolding. Surfaces treated before erection do not require scaffolding.

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Corrosion science is probably unique in crossing the borders of almost all technologies and since 1963 'Corrosion' has been the leading source of information on the subject. It provides an encyclopedic coverage of corrosion science and technology and is an essential first point of reference for everyone in the field. The science has advanced significantly in the seventeen years since the publication of the second edition and this new edition has been thoroughly updated to reflect this.

'Corrosion' is a two-volume reference work embracing a vast range of topics including high-temperature and aqueous corrosion and their control. It was first published in 1963 by George Newnes Ltd and over the years it has gained an international reputation. This edition extends to over 2700 pages, and contains 138 sections all written by specialists. It follows the format of previous editions; some sections have been completely rewritten, whilst others have been altered and extended. New sections have been added to cover areas not previously included.

Lionel Shreir, who edited the first two editions, has been joined by two editors, *Ray Jarman* and *Tim Burstein*, to produce the third edition of this unique work. Although he did not live to see its publication it is hoped that the book serves as a fitting tribute to his memory.

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Introduction; Design and economic aspects of corrosion; Cathodic and anodic protection; Pretreatment design for metal finishing; Methods of applying metallic coatings; Protection by metallic coatings; Protection by paint coatings; Chemical conversion coatings; Miscellaneous coatings; Conditioning the environment; Non-metallic materials; Corrosion testing, monitoring and inspection; Electrochemistry and metallurgy relevant to corrosion; Useful information; Index.

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